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SEARCH FOR PHYSIOLOGICALLY ACTIVE COMPOUNDS

Part II. Synthesis of 7-Amino and 7-Halo-4-Methyl Coumarins

By N. V. Subba Rao and V. Sundaramurthy

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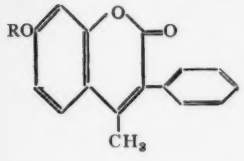
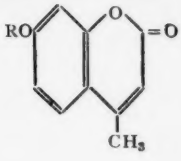
Received February 14, 1956

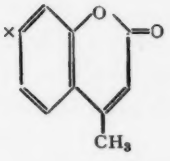
Seshadri and Varadarajan[1] reported that 3-phenyl-4-methyl umbelliferrone (I *a*) and its methyl ether (I *b*) were comparatively more toxic to fish than the corresponding 4-methyl umbelliferrone (II *a*) or its methyl ether (II *b*). Later Rao and Sundaramurthy[2] observed that the toxic properties were considerably enhanced if the hydroxyl of 3-phenyl-4-methyl umbelliferrone is replaced by halogen group. In order to verify whether this is always true in other cases and also to establish the superior toxic properties of the 3-phenyl substituent in the coumarins, it has been considered desirable to synthesise 7-halo-4-methyl coumarins (III) and compare their physiological activity with the corresponding 3-phenyl coumarins and also with the 7-hydroxy and 7-methoxy-4-methyl coumarins.



I (*a*) R=H
(*b*) R=CH_3



II (*a*) R=H
(*b*) R=CH_3



III X = Cl, Br, I

Clayton[3] prepared the 7-chloro-4-methyl coumarin by the Pechmann condensation of *m*-chloro phenol. But the 7-bromo and 7-iodo-4-methyl coumarins do not seem to have been prepared so far. Since the *m*-halo phenols are not easily accessible and by Pechmann condensation give very poor yields of the coumarins, the direct condensation procedures have been found to be unsuitable for the preparation of the above compounds. It was, however, found convenient to synthesise the 7-amino-4-methyl coumarin and from it the corresponding 7-halo-4-methyl coumarins following the procedure already adopted by us in the synthesis of 7-halo-4-methyl-3-phenyl coumarins.[2] As the direct condensation of *m*-amino phenol with ethyl acetoacetate in the presence of anhydrous zinc chloride, adopted by Pechmann,[4] gave rise to some difficulties in the isolation of the final product,

the condensation has been improved making use of *m*-acetamino phenol instead of amino phenol and phosphorous oxychloride as the condensing agent. The 7-acetamino-4-methyl coumarin obtained in good yield by this method was later hydrolysed to the corresponding 7-amino compound with alcoholic hydrochloric acid. From the amino compound the 7-halo-4-methyl coumarins have been prepared by diazotisation followed by Sandmeyer reaction. 7-Chloro-4-methyl coumarin obtained by this procedure has been found to be identical with that obtained by the Pechmann condensation of *m*-chloro phenol.

Though the 7-amino-4-methyl coumarin did not possess appreciable toxicity to fish, the 7-halo-4-methyl coumarins were comparatively more toxic than the corresponding methoxy compound and far weaker than the 7-halo-4-methyl-3-phenyl coumarins.

EXPERIMENTAL

(*i*) 7-*Amino*-4-*methyl coumarin*

m-Acetamino phenol (10 g.), ethyl acetoacetate (10 ml.) and phosphorous oxychloride (2·5 ml.) were heated on a water-bath for 1 hr., kept overnight and poured in ice-cold water. The 7-acetamino-4-methyl coumarin that separated was filtered, washed with water, dried (4 g.) and on recrystallisation from alcohol gave colourless plates, m.p. 270° C., which agreed in all its properties with that prepared by Pechmann through acetylation of 7-amino-4-methyl coumarin.

The acetamino coumarin (4 g.) was refluxed with alcoholic hydrochloric acid (2 : 1, 50 ml.) for 2 hrs., cooled, diluted with water and neutralised with 5% alkali. The compound that separated (2·8 g.) was recrystallised from alcohol when cream coloured glistening needles were obtained, m.p. 226° C. (Pechmann, 219–23° C.). (Found: C, 68·3; H, 5·6; N, 7·9; $C_{10}H_9O_2N$ requires C, 68·6; H, 5·2; N, 8·0%.)

(*ii*) 7-*Chloro*-4-*methyl coumarin*

7-Amino-4-methyl coumarin (0·2 g.) was dissolved in 4 N hydrochloric acid (20 ml.) and diazotised with sodium nitrite (0·1 g. in 5 ml. water) at 0–5° C. After standing for 1 hr., the cold diazonium solution was added to an ice-cold solution of cuprous chloride (1 g. in 5 ml. conc. hydrochloric acid) with vigorous stirring. The reaction mixture was allowed to attain room temperature and then warmed on a water-bath at 60° C. till frothing subsided. The 7-chloro-4-methyl coumarin that separated (0·1 g.) was collected and on recrystallisation from aqueous alcohol gave colourless needles; m.p. 144° C. Mixed melting point of the substance with the one prepared

following Clayton's procedure was not depressed. (Found: C, 61·8; H, 3·8; Cl, 18·3; $C_{10}H_7O_2Cl$ requires C, 61·7; H, 3·6; Cl, 18·1%.)

(*iii*) *7-Bromo-4-methyl coumarin*

The cold diazonium solution obtained from 7-amino-4-methyl coumarin (0·2 g.) was added to a cold solution of cuprous bromide (1 g. in 5 ml. of hydrobromic acid) gradually with mechanical stirring and the precipitate obtained (0·08 g.) was worked up as above. The 7-bromo-4-methyl coumarin on recrystallisation from aqueous alcohol gave pale yellow needles; m.p. 135° C. (Found: C, 50·7; H, 3·2; Br, 31·8; $C_{10}H_7O_2Br$ requires C, 50·4; H, 2·9 ; Br, 31·1%).

(*iv*) *7-Iodo-4-methyl coumarin*

The cold diazonium solution obtained from 7-amino-4-methyl coumarin (0·2 g.) was stirred with potassium iodide solution (1 g. in 5 ml. water) and the precipitate obtained (0·1 g.) was worked up as usual. The product on recrystallisation from aqueous alcohol gave light grey needles; m.p. 157° C. (Found: C, 41·8; H, 2·8; I, 43·6; $C_{10}H_7O_2I$ requires C, 41·8; H, 2·4; I, 44·4%.)

Summary

An improved method for the preparation of 7-amino-4-methyl coumarin is described. The corresponding halo-substituted coumarins prepared from the amino compound by diazotisation and Sandmeyer reaction have been found to be more toxic to fish than the 7-methoxy-4-methyl coumarin and far less toxic than the corresponding 3-phenyl coumarins.

We thank Mr. C. V. Ratnam for the micro-analyses recorded in the paper.

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4. Pechmann .. *Ber.*, 1899, **32**, 3681.

X-RAY DIFFRACTION BY BINARY LIQUID MIXTURES: PYRIDINE-FATTY ACID SYSTEMS

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Received February 16, 1956

(Communicated by Prof. R. S. Krishnan, F.A.SC.)

1. Introduction

It is well known that in certain binary liquid mixturs, a strong interaction between the molecules of the component liquids gives rise to association. Such an association is termed complex formation the extent of which depends not only on the nature of the constituent liquids but also on their relative concentrations. The existence of complexes of the type C_5H_5N—nRCOOH in pyridine-fatty acid systems has been inferred from the occurrence of singularities in their physical properties such as viscosity (Tsakalatos, 1908), refractive index (Pushin and Matavulj, 1932), adiabatic compressibility (Balachandran, 1954), etc. The results obtained by the author (1954) from studies on the Raman spectra of mixtures containing pyridine as one of the components and formic, acetic, propionic or butyric acid as the other component also confirmed the existence of such complexes. In the present investigation, the diffraction of X-rays by three binary liquid mixtures, *viz.*, pyridine-formic acid, pyridine-acetic acid, and pyridine-propionic acid, has been studied and the results obtained have been discussed in relation to the complex formation.

2. Experimental

The liquids used were either Merck's or Kahlbaum or Baker's analytical reagents and were further purified by distillation. Seven mixtures were prepared for each acid, the concentrations by weight being respectively 20, 30, 50, 60, 70, 80 and 90 mol.%. The X-rays employed were the filtered CuK α radiations from a Seifert tube operated at 32 K.V. The current in the X-ray tube was maintained at about 16 m.a. A fine beam of X-rays collimated by a system of circular lead apertures (1/32″) passed through the specimen under investigation and fell upon an Ilflex X-ray film kept at a distance of 5 cm. from the specimen. The mixture was contained in a very thin-walled glass tube which did not give any appreciable diffraction pattern of its own in two hours. A thick lead disc of appropriate diameter was fixed in front of the film to cut off the undeviated beam of X-rays in order to avoid

fogging of the film by over-exposure. An exposure of two hours was necessary to get an intense diffraction photograph, the exposure being kept constant for the pure liquids and mixtures.

3. Results and Discussion

The difiraction photographs of the component liquids and their mixtures are reproduced in Figs. 1, 2 and 3 on Plates (IX–XI). The mean diameters of the diffraction rings were measured in the usual way and the values of the spacings a_1 and a_2 corresponding to the outer and inner diffraction rings have been calculated using the well-known Bragg formula. The values are given in Table I. F, A and P refer respectively to the systems Pyridine-Formic acid, Pyridine-Acetic acid and Pyridine-Propionic acid.

Table I

Concentration in mol. % acid	a_1 in Å u.			a_2 in Å u.		
	F.	A.	P.	F.	A.	P.
0 (Pyridine)	4·69	4·69	4·69	..	..	..
20	4·59	4·66	4·66	9·7	9·44	9·27
30	4·48	4·59	4·66	9·7	9·44	9·27
50	4·24	4·51	4·59	8·89	8·89	9·27
60	4·19	4·48	4·59	8·53	8·66	8·77
70	4·05	4·39	4·51	8·41	8·66	8·77
80	3·86	4·31	4·48	7·79	8·21	8·41
90	3·70	4·21	4·48	7·79	7·79	8·41
100 (acid)	3·67	4·16	4·48	7·45	7·20	8·00

An examination of the photographs reproduced on Plates (IX–XI) reveals that these mixtures behave in a similar fashion towards X-ray diffraction. While pyridine gives a strong, sharp, single diffraction ring, the patterns for the acids consist of a major intensity maximum followed by a much less intense one at a smaller angle. The diffraction pattern for the mixture is not a super-position of the patterns for the component liquids. The variation in the value of a_1, the spacing corresponding to the principal maximum, with concentration of the acid has been graphically represented for these

mixtures in Fig. 4. Unlike in the cases of many mixtures where the sapcing due to the principal diffraction ring varies continuously between the two values due to the individual components, in the case of pyridine-fatty acid systems under examination the spacing *vs.* concentration curves exhibit points of inflexion. The presence of these points of inflexion is indicative of the existence of complexes in these mixtures. A similar observation has been reported by Banerjee (1929) from a study of the X-ray diffraction of alloys of sodium and potassium.

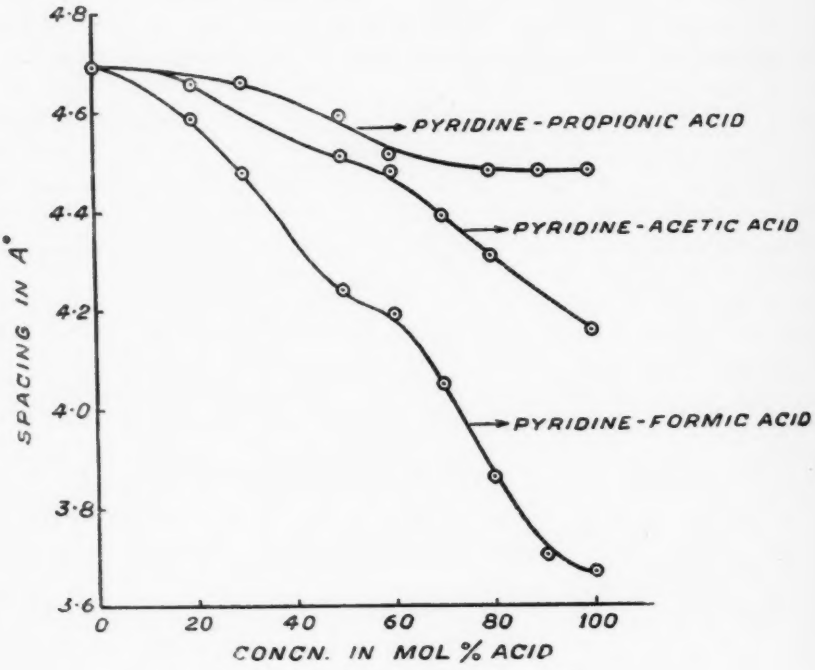

FIG. 4. Spacing *vs.* Concn. curves

The diffraction patterns for the mixtures show a second ring also at all concentrations. The presence of this ring is rather interesting. The inner ring in the pure acids has been ascribed by several workers to the existence of double molecules of these acids in the pure state, arranged end to end and providing an additional set of planes responsible for the X-ray diffraction at smaller angles. In the case of the pyridine-fatty acid mixtures, it is difficult to attribute the second ring to the continued existence of these dimers since the inner ring in acetic acid has been shown by Krishnamurthy (1930)

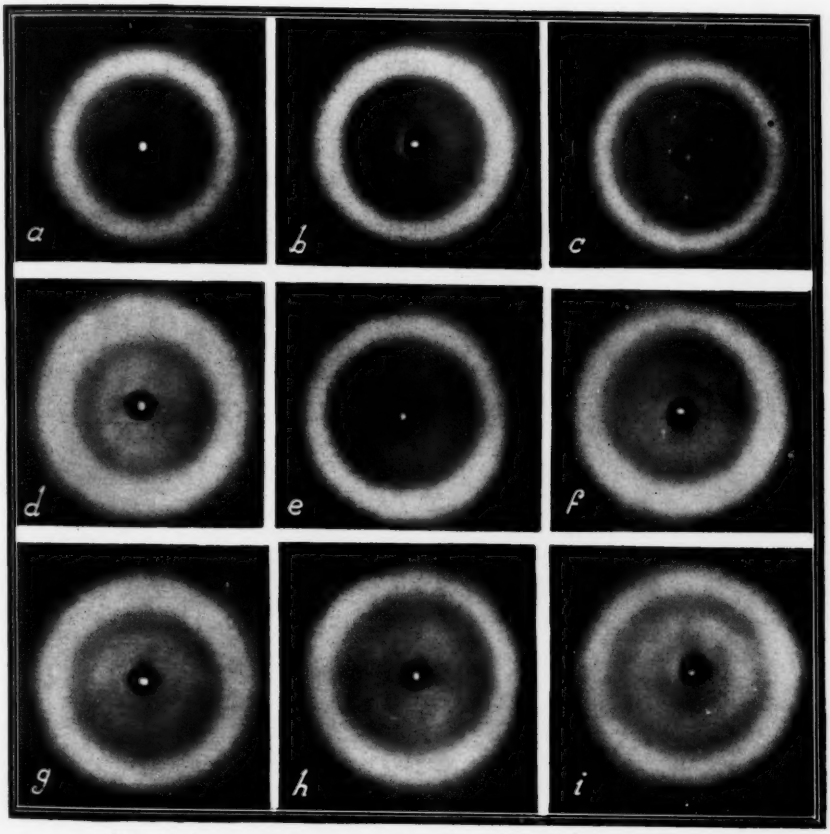

FIG. 1. X-ray diffraction pattern of a mixture of pyridine and formic acid

a–pyridine	*b*–20 mol % acid	*c*–30 mol % acid
d–50 mol % acid	*e*–60 mol % acid	*f*–70 mol % acid
g–80 mol % acid	*h*–90 mol % acid	*i*–formic acid

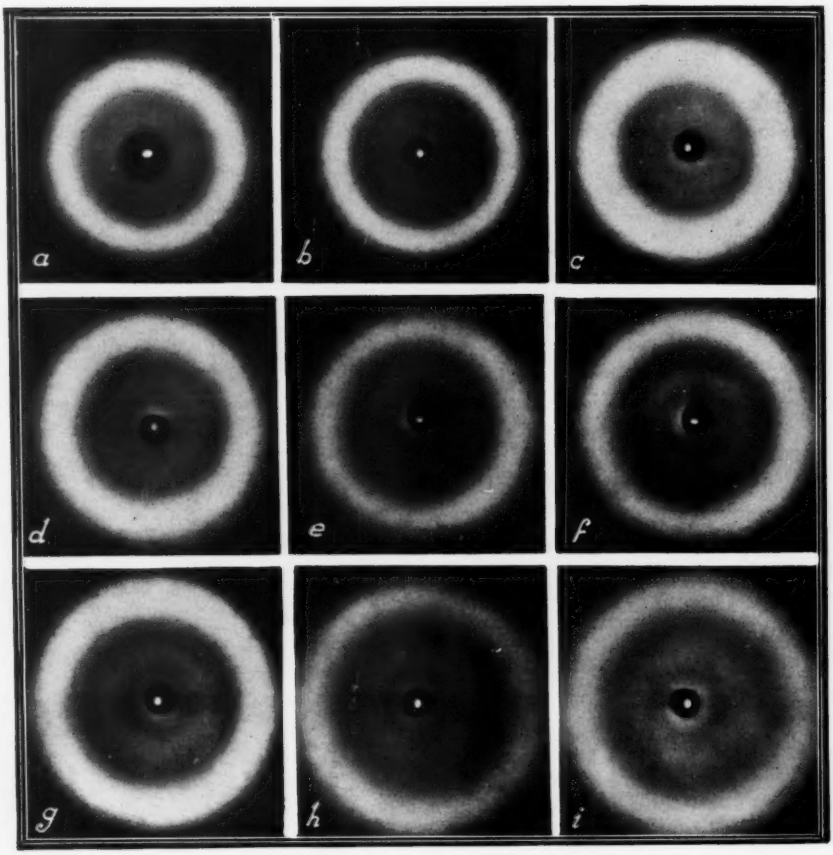

FIG. 2. X-ray diffraction pattern of a mixture of pyridine and acetic acid.

a–pyridine	*b*–20 mol% acid	*c*–30 mol% acid
d–50 mol% acid	*e*–60 mol% acid	*f*–70 mol% acid
g–80 mol% acid	*h*–90 mol% acid	*i*– acetic acid

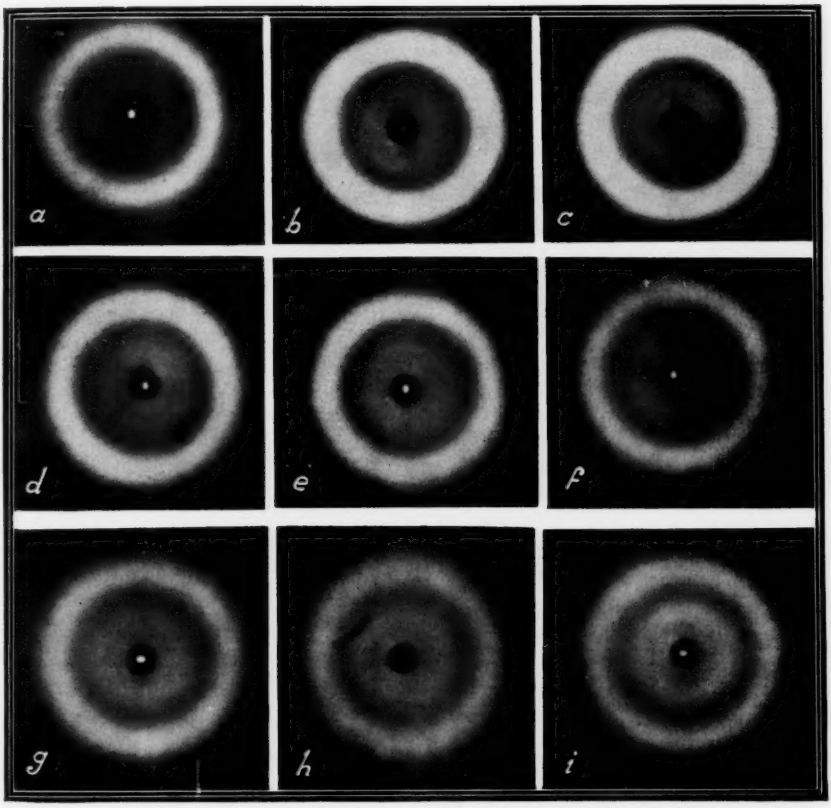

FIG. 3. X-ray diffraction pattern of a mixture of pyridine and propionic acid

a–pyridine	*b*–20 mol% acid	*c*–30 mol% acid
d–50 mol% acid	*e*–60 mol% acid	*f*–70 mol% acid
g–80 mol% acid	*h*–90 mol% acid	*i*–propionic acid

to disappear even in very concentrated solution with water, a much weaker solvent than pyridine. The spacing *vs.* concentration curves (not reproduced here) corresponding to the inner ring also show points of inflexion. This seems to be an additional evidence for the presence of complexes in these mixtures.

The author records his thanks to Prof. R. S. Krishnan for his guidance and interest in the work. His thanks are also due to Dr. S. Ramaseshan and Dr. P. S. Narayanan for the many valuable help he received from them.

Summary

X-ray diffraction by three binary liquid systems, *viz.*, Pyridine-Formic acid, Pyridine-Acetic acid and Pyridine-Propionic acid, have been investigated over a range of concentrations. The spacings calculated from the Bragg formula corresponding to the two diffraction maxima observed in these mixtures have been tabulated. The spacing *vs.* concentration curves in all the three mixtures show certain points of inflexion. These have been attributed to complex formation in them.

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INFRA-RED INVESTIGATIONS ON THE HYDROCARBON CYPERENE—II

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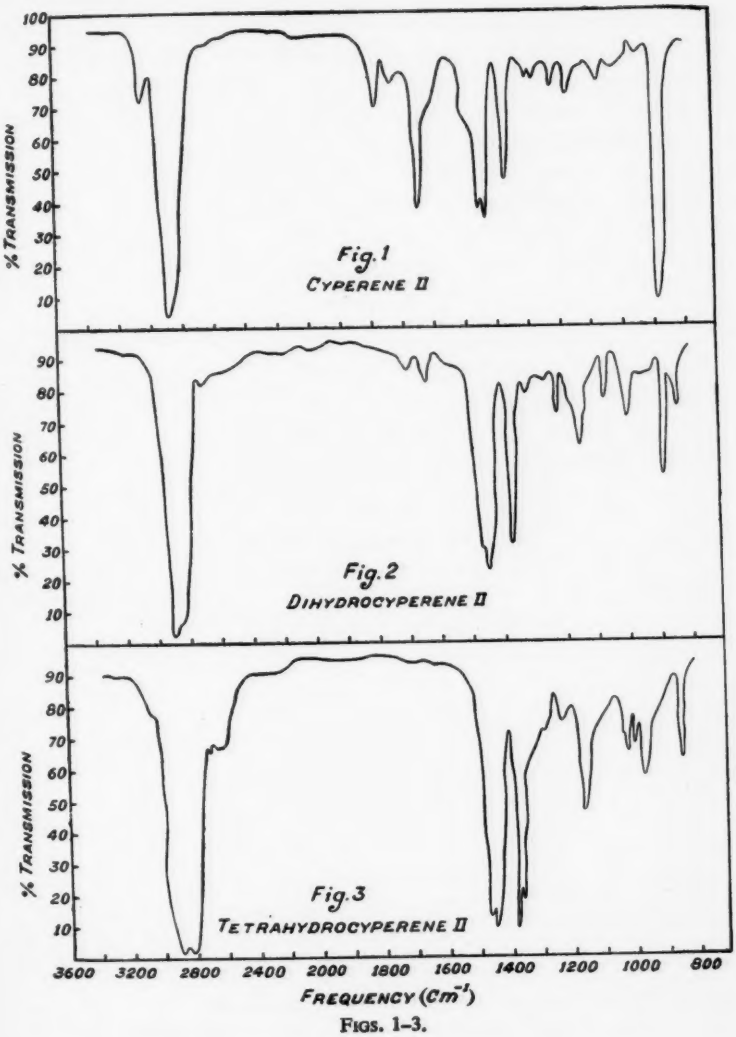
(Communicated by Prof. R. S. Krishnan, F.A.SC.)

1. Introduction

Kimura and Ohtani (1928) gave the name cyperene to the hydrocarbon fraction of the oil extracted from the tubers of the weed plant *Cyperus rotendus* L. Subsequently Hegde and Rao (1935) followed up these investigations on the Indian variety but failed to confirm the presence of a hydrocarbon with properties ascribed by Kimura and Ohtani. Hegde and Rao, therefore, suggested that there were at least two different hydrocarbons present in the oil extracted from *Cyperus rotendus* L. Recently one of us (Senich) has carried out a systematic examination of the hydrocarbon fraction of the oil from Indian tubers (Madras variety) and it has been found that by fractional distillation four different hydrocarbon fractions could be obtained. Two of these fractions could be obtained in yields of 14% and 6% while the other two fractions are obtainable in much lower yields. The product which is available in maximum yield (14%) has been named cyperene II (M. Wt. 204). In this paper we shall describe the results of our investigations on the infra-red spectra of cyperene II and its hydrogenated products. However, before doing so it will be desirable to note the following facts regarding the chemical properties of these compounds which will enable us to discuss the structure of these molecules from the infra-red data.

Even after hydrogenation with $Pd(OH)_2$ as catalyst, cyperene II reacts to tests for unsaturation (tetranitromethane), that is, the compound shows the presence of more than one unsaturated bond in the molecule. However, after hydrogenation with PtO_2 as catalyst and acetic acid as solvent, the compound becomes completely saturated and thus the presence of two unsaturated bonds in the molecule was inferred. The product obtained after hydrogenation by $Pd(OH)_2$ as catalyst is termed as dihydrocyperene II (M. Wt. 206), while the completely hydrogenated product is termed as tertrahydrocyperene II

(M. Wt. 208). The chemical investigations on these compounds which will be published elsewhere, have shown that the skeletal structure of these compounds is the same as that of eudalene. Since the infra-red spectra of these hydrocarbons can give us valuable evidence regarding molecular structure we have undertaken the study of the same and in what follows it will be seen that certain important conclusions can be arrived at from these studies. It



FIGS. 1–3.

may be noted here that the Raman spectra of these compounds have already been studied by Hariharan and Senich (1955).

2. EXPERIMENTAL

The compounds were examined in the form of thin liquid films between NaCl windows separated by a spacer 0·012 mm. thick. A Perkin-Elmer model 112 single beam double pass infra-red spectrometer with NaCl optics was used for recording the spectra. The region examined was between 800 and 3,500 cm.$^{-1}$ and the resolution with the slit width employed was approximately as follows: 800–1,500 cm.$^{-1}$ — 4 cm.$^{-1}$; 1,500–2,000 cm.$^{-1}$ — 8 cm.$^{-1}$; 2,000–3,500 — 20 cm.$^{-1}$ The liquids were freshly distilled over sodium before examination. Owing to their high boiling points (cyperene II — 129° C. at 10 mm.) trouble on account of evaporation in the cell was absent. Some of the physical properties of these compounds are listed here. Cyperence II — n_D^{30} 1·5072; α_D^{30} + 13° 48′. Dihydrocyperene II n_D^{25} 1·4920; α_D^{25} + 12° 0′. Tetrahydrocyperene II n_D^{25} 1·4838; α_D^{25} + 1° 24′.

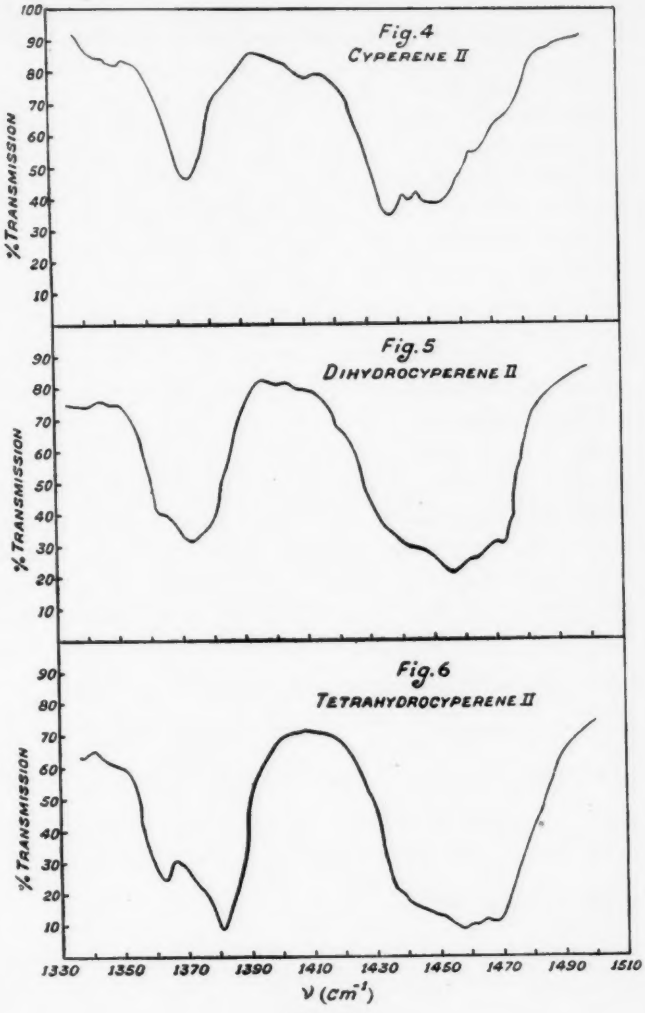
3. RESULTS

In Figs. 1, 2 and 3 are reproduced the infra-red spectra of cyperene II, dihydrocyperene II and tetrahydrocyperene II respectively. Figs. 4, 5 and 6 show the enlarged spectra in the region 1,330 — 1,500 cm.$^{-1}$ so as to bring out the details which are discussed later. Table I summarises the infra-red data on these compounds.

TABLE I

Infra-red absorption frequencies

Cyperene II	Dihydrocyperene II	Tetrahydrocyperene II
858 (W)	847 (W)	855 (W)
886 (*S*)	*885* (*M*)	*978* (*M*)
1070 (W)	1001 (W)	1100
1171 (W)	1072 (W)	1030
1220 (W)	1151 (W)	*1164* (*S*)
1372 (*S*)	1222 (W)	1224
	1373 (*S*)	*1367/1381* (*S*)
1436/1452 (*S*)	*1456/1472* (*S*)	*1458* (*S*)
1644 (*S*)	*1644* (*W*)	
1728 (W)		2640 (W)
1775 (W)	2700 (W)	2700 (W)
2890 (*S*)	*2890* (*S*)	*2820/2900* (*S*)
3050 (W)		



FIGS. 4–6.

4. DISCUSSION

The appearance of a strong absorption band at 886 cm.$^{-1}$ in cyperene II clearly indicates the presence of the grouping $\diagdown$C=CH$_2$ since this frequency is easily ascribed to the C—H out of plane deformation in this group especially on account of its intensity (Bellamy, 1954). In dihydrocyperene II this

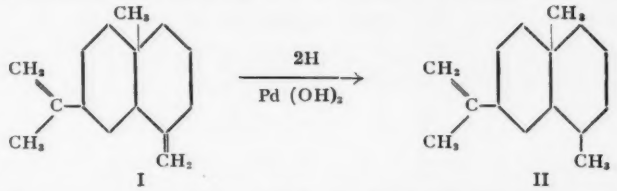
band is no doubt present but is very much less intense while in the completely hydrogenated compound this band is absent. (Compare Figs. 1, 2 and 3). A corroboration of this fact can also be obtained from the C=C stretching frequency of 1,644 cm.$^{-1}$ in the abovementioned grouping (Sheppard and Simpson, 1952). The absence of this band in tetrahydrocyperene is noteworthy. It will be seen that remarks made earlier regarding the intensity of the 886 cm.$^{-1}$ band apply equally to the 1,644 cm.$^{-1}$ band also. These facts are in good agreement with the chemical point of view, *viz.*, that hydrogenation of cyperene II removes in the first instance one of the two double bonds while in the last case the compound (tetrahydro-) is completely saturated and hence shows no absorption in these regions. It will be shown subsequently that this proof of the presence of the grouping $\diagdown\!\!\diagup C{=}CH_2$ in cyperene II and in dihydrocyperene II goes a long way in elucidating the structure of these molecules.

The 1,370 cm.$^{-1}$ band in cyperene II and in dihydrocyperene II can be ascribed to the symmetrical deformation mode of the C—CH_3 group. In the dihydrogenated compound this band appears with greater intensity while in the tetrahydrogenated compound some additional features are to be noticed (compare Figs. 4, 5 and 6). The 1,370 cm.$^{-1}$ absorption band of tetrahydrocyperene II has two sharp peaks, the positions of which are 1,363 and 1,381 cm.$^{-1}$ respectively. These arise from the resonance splitting of the C—H deformation frequencies of the two C—CH_3 groups in $-HC\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$ (McMurray and Thornton, 1952; Sheppard and Simpson, 1953). The presence of a strong band at 1164 cm.$^{-1}$ (skeletal vibration of $-HC\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$) in the completely saturated compound is again in agreement with this assignment. We may, therefore, conclude that the molecule of tetrahydrocyperene II contains the grouping $-HC\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$.

The symmetrical mode of the C—H vibration in C—CH_3 group generally gives rise to a broad band near 1,450 cm.$^{-1}$ The appearance of this band in the three compounds studied and the increase in intensity of this band with hydrogenation point out to the increase in the number of methyl groups. The intense absorption band near 2,890 cm.$^{-1}$ has a very broad coverage and on account of the lower resolution (20 cm.$^{-1}$) of the spectrometer in this region and owing to the overlapping of the C—H stretching frequencies of CH_3, CH_2 and CH (tertiary) groupings it is very difficult to differentiate these frequencies. Generally speaking this band is to be ascribed

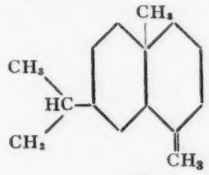
to the C—H stretching frequencies and here again the qualitative correlation in intensity with progressive hydrogenation is clearly seen.

Having discussed the main features of the infra-red spectra of these three compounds it now remains for us to see how best the observed spectra could be correlated to the molecular structures. It was stated earlier that the chemical evidence points out to the skeletal structure of eudalene for these molecules. Based on this we can now postulate for cyperene II structure I which on hydrogenation first gives dihydrocyperene II (struc-



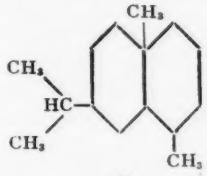
I II

ture II). The appearance of two kinks in the 1,370 cm.$^{-1}$ band of dihydrocyperene II may be due to the formation of (III) but this is certainly extre-



III

mely small and the evidence is mainly spectroscopic. The structure of



IV

tetrahydrocyperene II can be, therefore, given by IV. Other structures with double bond inside the ring can be postulated for cyperene II but the infra-red spectral data do not then lend themselves to satisfactory interpretation. Particular mention should be made of the $\diagdown C = CH_2$ group and its strong intensity and the resonance splitting of the 1,370 cm.$^{-1}$ band due to the $-HC\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix}$ grouping with its appearance in the tetrahydrogenated compound.

Structure I accounts satisfactorily for the following bands. 886 cm.$^{-1}$; 1,372 cm.$^{-1}$; 1,430–1,450 cm.$^{-1}$; 1,644 cm.$^{-1}$ and 2,890 cm.$^{-1}$—in fact for all the observed strong infra-red bands. Structure II accounts for the following bands: 885 cm.$^{-1}$, 1,373 cm.$^{-1}$; 1,430–1,450 cm.$^{-1}$ and 2,890 cm.$^{-1}$ It also accounts for the decrease in the intensity of the 885 cm.$^{-1}$, the persistence of the weak 1,644 cm.$^{-1}$ band and the increase in intensity of the 1,373 cm.$^{-1}$ band. Even the presence of the two kinks (see Fig. 5) in the 1,373 cm.$^{-1}$ band of this compound (dihydro-) may be accounted for on the basis of the presence of traces of III formed from I during hydrogenation. Structure IV accounts completely for the observed infra-red spectrum of tetra-hydrocyperene II and in particular for the appearance of the two maxima in the 1,370 cm.$^{-1}$ band and its increase in intensity.

5. SUMMARY

The infra-red spectra of cyperene II [hydrocarbon isolated from oil extracted from *Cyperus rotendus* (Indian variety)], dihydrocyperene II and tetrahydrocyperene II have been studied in the form of thin liquid films in the region 800–3,500 cm.$^{-1}$ The skeletal structure of the molecules is of the eudalene type. The probable structures of these molecules are discussed in the light of the infra-red data and tentative assignments have been made.

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ON TWO TAUBERIAN THEOREMS FOR THE BOREL TRANSFORM OF A SEQUENCE

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1. Introduction

If s_n, $n = 0, 1, 2, \cdots$, is a real sequence and its Abel transform is denoted by

$$A(x) \equiv (1 - e^{-1/x}) \sum_{n=0}^{\infty} e^{-n/x}, \qquad 0 < x < \infty, \tag{1}$$

then the inequalities for s_M as $M \to \infty$ in the following two theorems, the first due to Karamata ([2] p. 66) and the second to Pennington ([3] Theorem 4), are results following from the assumption that $A(x)$ is bounded on one side as $x \to \infty$ and s_n satisfies a suitable one-sided Tauberian condition, e.g. the assumption $A(x) = O_R(1)$ as $x \to \infty$ and $s_n - s_{n-1} = O_L(\lambda_n^{-1})$ as $n \to \infty$ where λ_n is of the type $\lambda_n \uparrow \infty$. These two theorems, in the special case of s_n "infinitely summable" by the Abel transform, e.g. the case $A(x) \to -\infty$ as $x \to \infty$, were originally given by the first of the two present authors ([5] Theorems 8, 3*a*), while the connexion between the theorems, extended to a certain class of transforms, was indicated by the second author ([4] Proofs of Theorems A, C).

Theorem 1 (A). *If $\{s_n\}$ is a real sequence such that*

$$s_n - s_{n-1} \geqslant -W/n, \quad n \geqslant 1, \quad 0 \leqslant W < \infty, \tag{$T_{1(A)}$}$$

and if $A(x)$ defined by (1) *is subject to the condition*

$$A(x) < O(1), \quad x \to \infty,$$

then

$$s_M \leqslant W \log\log M + O(1), \quad M \to \infty.$$

Theorem 2 (A). *If, in Theorem* 1 (A), *The Tauberian condition* ($T_{1(A)}$) *is replaced by*

$$\lim_{n \to \infty} (s_n - s_{n-1})\, n \log\log n = -W, \quad 0 \leqslant W < \infty, \tag{$T_{2(A)}$}$$

* My collaborator passed away on the 20th April 1955, and it is now my sad duty to publish some of the work which he and I had jointly planned.—C.T.R.

the condition on $A(x)$, i.e. $A(x) < O(1)$, remaining unaltered, then the conclusion is altered to

$$\lim_{M\to\infty} \{A(M \log^{\mu} M) - s_M\} \geqslant -\mu W,\ \mu \geqslant 1.$$

In a paper not yet published,[6] the authors have obtained certain general theorems which may be placed alongside of a theorem attributed to the first author by Hardy ([1] Theorem 238†) and which includes Theorems 1 (A) and 2 (A) as well as their analogues, stated below as Theorems 1 (B) and 2 (B), for the Borel transform $B(x)$ of $\{s_n\}$ defined thus:

$$B(x) \equiv \sum_{n=0}^{\infty} e^{-x} \frac{x^n}{n!} s_n, \qquad 0 < x < \infty. \tag{2}$$

THEOREM 1 (B). *If $\{s_n\}$ is a real sequence for which*

$$s_n - s_{n-1} \geqslant -\tfrac{1}{2} W/\sqrt{n},\quad n \geqslant 1,\ 0 \leqslant W < \infty, \tag{$T_{1(B)}$}$$

and $B(x)$ in (2) satisfies the condition

$$B(x) < O(1),\ x \to \infty,$$

then

$$s_M \leqslant \tfrac{1}{2} W \sqrt{\log M} + O(1),\ M \to \infty.$$

THEOREM 2 (B). *If, in Theorem 1 (B), the Tauberian condition ($T_{1(B)}$) is replaced by*

$$\lim_{n\to\infty} (s_n - s_{n-1}) \sqrt{(n \log n)} = -W,\ 0 \leqslant W < \infty, \tag{$T_{2(B)}$}$$

the condition $B(x) < O(1)$ remaining unchanged, then the conclusion is changed to

$$\lim_{M\to\infty} \{B(M + 2\mu \sqrt{M \log M}) - s_M\} \geqslant -2\mu W,\ \mu \geqslant \tfrac{1}{2}.$$

It is known that the Tauberian condition ($T_{2(A)}$) in Theorem 2 (A) is the best-possible ([3] pp. 563–64) and that the upper estimate for s_M in the conclusion of Theorem 1 (A) cannot be brought down by an alteration of its dominant term, $W \log \log M$ ([2] §§ 1, 2). Similar remarks apply to Theorems 2 (B) and 1 (B) though they are naturally less easy to demonstrate than the remarks in respect of Theorems 2 (A) and 1 (A). The purpose of this note is to establish, by examples, the best-possible character of each of Theorems 2 (B) and 1 (B) in the senses indicated just now.

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† This theorem shows that, if either $A(x) = O(1)$ in Theorem 1 (A) or $B(x) = O(1)$ in Theorem 1 (B), then $s_M = O(1)$ in both Theorems 1 (A) and 1 (B).

2. Some Lemmas

The following lemmas are required for the purpose we have in view.

Lemma I. *If* $|h| \leqslant x^{\zeta}$, $1/2 < \zeta < 2/3$, *then*

$$\frac{e^{-x}\,x^{x+h}}{\Gamma(x+h+1)} = \sqrt{\left(\frac{1}{2\pi x}\right)}\,e^{-h^2/2x}\left\{1 + O\left(\frac{|h|+1}{x}\right) + O\left(\frac{|h|^3}{x^2}\right)\right\},\ x\to\infty.$$

This is a useful result whose proof is straightforward [1 Theorem 137, (5)].

Lemma II.

$$\sum_{0}^{M-[\sqrt{M\log M}]} e^{-M}\,\frac{M^n}{n!} = O\left(\frac{1}{M^{1/2}}\right),\ M\to\infty,$$

the symbol $[x]$ *used here and elsewhere, with reference to any* $x > 0$, *denoting the greatest integer not exceeding* x.

Lemma II is proved by breaking up the sum in it into component sums each of which excepting the last contains $[\sqrt{M}]$ terms, and then obtaining an upper estimate of each component sum, by Lemma I, in terms of

$[\sqrt{M}]$ {the largest, i.e. the first, term in the component sum}.

The details of the proof, to suit a slight modification of Lemma II, but adaptable to Lemma II, appear elsewhere [6 Lemma I, (16)].

Lemma III.

$$e^{-x}\sum_{1}^{\infty}|\sqrt{n}-\sqrt{N}|\,\frac{x^n}{n!} < \frac{|N-x|}{\sqrt{N}} + 2e^{-x}\sqrt{N}\,\frac{x^N}{N!}.$$

To prove Lemma III we start with the inequality

$$e^{-x}\sum_{1}^{\infty}|\sqrt{n}-\sqrt{N}|\,\frac{x^n}{n!} < \frac{e^{-x}}{\sqrt{N}}\sum_{0}^{\infty}|n-N|\,\frac{x^n}{n!}$$

and suitably rearrange the terms on the right.

3. 'Best-possible' Character of Theorem 2 (B)

The Tauberian condition $(T_{2(B)})$ in Theorem 2 (B) is the best possible in the sense that its replacement by

$$\lim_{n\to\infty}\frac{(s_n - s_{n-1})\sqrt{(n\log n)}}{f(n)} = -W,\quad 0 \leqslant W < \infty,$$

where $f(x)$ is any given function of $x > 0$ tending to ∞ with x, may involve, as in the example below,

$$B(x) - s_M \to -\infty$$

when $M \to \infty$ through a sequence of values $\{M_r\}$ such that

$$0 < M_1 < M_2 < \ldots . < M_r,\ M_r \to \infty\ (r \to \infty),$$

irrespective of the manner in which $x \to \infty$.

EXAMPLE 2 (B). *Suppose that*

$$M_1 = 2,\ M_r = M^2_{r-1} \text{ for } r \geqslant 2,$$

$$s_0 = s_1 = s_2 = 0,\ s_n - s_{n-1} = -\frac{f(n)}{\sqrt{(n \log n)}} \text{ for } 2 < n \neq M_r,\ r \geqslant 2,$$

$$s_{M_r} = 0,\ \textit{i.e.}\ s_{M_r} - s_{M_r-1} = \sum_{(\nu)} \frac{f(\nu)}{\sqrt{(\nu \log \nu)}},\ M_{r-1} < \nu < M_r,\ r \geqslant 2.$$

Then

$$B(x) - s_{M_r} = B(x) \to -\infty,\ x \to \infty.$$

Proof.—We may suppose that $f(x)$ is monotonic increasing (as well as positive) for all large x since, otherwise, $f(M_{r-1})$ in (3) below will be replaced by $\min f(n)$ for $M_{r-1} < n < M_r$ with corresponding replacements elsewhere but no modification in principle.

We first observe that $s_n \leqslant 0$ for all n, and that, for $M_{r-1} < n < M_r$, r sufficiently large,

$$s_n = \sum_{M_{r-1}}^{n-1} (s_{\nu+1} - s_\nu) = -\sum_{M_{r-1}}^{n-1} \frac{f(\nu+1)}{\sqrt{\{(\nu+1)\log(\nu+1)\}}}$$

$$< -\frac{f(M_{r-1})(n - M_{r-1})}{\sqrt{(n \log n)}},$$

so that

$$s_n < -f(M_{r-1})\left\{\sqrt{\left(\frac{n}{\log n}\right)} - \sqrt{\left(\frac{M_{r-1}}{\log M_{r-1}}\right)}\right\}. \quad (3)$$

Let

$$x_r = M_r + (\sqrt{\log M_r} - 2)\sqrt{M_r}, \qquad d_r = [\sqrt{x_r}],$$

and, wherever necessary, let us consider only values of r after a stage, making $r \to \infty$ in obtaining certain upper or lower estimates. By (3),

$$B(x) \leqslant \sum_{M_r - d_r}^{M_r} e^{-x} \frac{x^n}{n!} s_n = \sum_{M_r - d_r}^{M_r - 1} e^{-x} \frac{x^n}{n!} s_n$$

$$< -\sum_{M_r - d_r}^{M_r - 1} e^{-x} \frac{x^n}{n!} f(M_{r-1}) \left\{\sqrt{\left(\frac{n}{\log n}\right)} - \sqrt{\left(\frac{M_{r-1}}{\log M_{r-1}}\right)}\right\}$$

$$< - f(M_{r-1}) \left\{ \sqrt{\left(\frac{M_r - d_r}{\log (M_r - d_r)}\right)} - \sqrt{\left(\frac{M_{r-1}}{\log M_{r-1}}\right)} \right\} \sum_{M_r - d_r}^{M_r - 1} e^{-x} \frac{x^n}{n!},$$

or $$B(x) < - f(M_{r-1}) \sqrt{\left(\frac{M_r}{\log M_r}\right)} \{1 + o(1)\} \sum_{M_r - d_r}^{M_r - 1} e^{-x} \frac{x^n}{n!}. \tag{4}$$

Case 1. $M_r \leqslant x \leqslant x_r$, $r \to \infty$.

$$\sum_{M_r - d_r}^{M_r - 1} e^{-x} \frac{x^n}{n!} \geqslant \sum_{M_r - d_r}^{M_r - 1} e^{-x_r} \frac{{x_r}^n}{n!} > d_r e^{-x_r} \frac{{x_r}^{M_r - d_r}}{\Gamma(M_r - d_r + 1)},$$

i.e. $$\sum_{M_r - d_r}^{M_r - 1} e^{-x} \frac{x^n}{n!} > d_r e^{-x_r} \frac{{x_r}^{x_r - h_r - d_r}}{\Gamma(x_r - h_r - d_r - 1)} \tag{5}$$

where

$$h_r = x_r - M_r = (\sqrt{\log M_r} - 2)\sqrt{M_r}.$$

Estimating the right-hand member of (5) by using Lemma I with $x = x_r$, $h = - h_r - d_r$, and taking into account the facts

$$\frac{{h_r}^2}{2x_r} = \frac{\log M_r}{2} + 2 - 2\sqrt{\log M_r} + o(1),$$

$$\frac{h_r d_r}{x_r} = \sqrt{\log M_r} - 2 + o(1), \qquad \frac{{d_r}^2}{2x_r} = \frac{1}{2} + o(1),$$

we get

$$\sum_{M_r - d_r}^{M_r - 1} e^{-x} \frac{x^n}{n!} > \frac{\{1 + o(1)\}}{\sqrt{(2\pi e)}} \frac{e^{\sqrt{\log M_r}}}{\sqrt{M_r}}. \tag{6}$$

Using (6) in (4), we at once conclude that

$$B(x) < - f(M_{r-1}) \sqrt{\left(\frac{M_r}{\log M_r}\right)} \frac{\{1 + o(1)\}}{\sqrt{(2\pi e)}} \frac{e^{\sqrt{\log M_r}}}{\sqrt{M_r}} \to - \infty.$$

Case 2. $x_r < x < M_{r+1}$, $r \to \infty$.

Clearly

$$B(x) \leqslant \sum_{(n)} e^{-x} \frac{x^n}{n!} s_n \tag{7}$$

for any $x > 0$ and n running through any values, and therefore for

$$M_r < x_r < x < M_{r+1},$$

$$M_r < [x] - [\sqrt{x}] \leqslant n \leqslant [x] - 1 < M_{r+1}.$$

In (7) with x and n restricted as above, we use

$$s_n \leqslant s_{[x]-[\sqrt{x}]} < -f(M_r)\left\{\sqrt{\left(\frac{[x]-[\sqrt{x}]}{\log([x]-[\sqrt{x}])}\right)}-\sqrt{\left(\frac{M_r}{\log M_r}\right)}\right\}$$

which follows from (3). Then

$$B(x) < -f(M_r)\left\{\sqrt{\left(\frac{[x]-[\sqrt{x}]}{\log([x]-[\sqrt{x}])}\right)}-\sqrt{\left(\frac{M_r}{\log M_r}\right)}\right\}\sum_{[x]-[\sqrt{x}]}^{[x]-1} e^{-x}\frac{x^n}{n!}$$

$$< -f(M_r)\{\ldots.\}\,[\sqrt{x}]\,e^{-x}\,\frac{x^{[x]-[\sqrt{x}]}}{([x]-[\sqrt{x}])!}$$

Now $\{\ldots.\}$ in the above expression is decreased when x is replaced by x_r since $\sqrt{(y/\log y)}$ increases with y for all large enough y. After effecting this replacement in $\{\ldots\}$ and applying the first mean-value theorem to $\{\ldots\}$, we obtain

$$B(x) < -f(M_r)\,\frac{[x_r]-[\sqrt{x_r}]-M_r}{2\sqrt{(\xi\log\xi)}}\{1+o(1)\}\,[\sqrt{x}]\,e^{-x}\,\frac{x^{[x]-[\sqrt{x_j}}}{([x]-[\sqrt{x}])!}$$

where

$$M_r < \xi < [x_r]-[\sqrt{x_r}],$$

i.e.

$$B(x) < -f(M_r)\,\frac{x_r-M_r}{2\sqrt{(M_r\log M_r)}}\,\frac{\{1+o(1)\}\sqrt{x}}{\sqrt{(2\pi xe)}},$$

or

$$B(x) < -\frac{f(M_r)}{2\sqrt{(2\pi e)}}\{1+o(1)\} \to -\infty.$$

This completes the proof of the result stated as Example 2 (B).

4. 'BEST-POSSIBLE' CHARACTER OF THEOREM 1 (B)

Theorem 1 (B) is the best possible under the conditions assumed since we can find a sequence $\{s_n\}$, of which an example is given below, fulfilling $(T_{1(B)})$ and such that $B(x) < O(1)$ as $x \to \infty$ while

$$s_{M_r} = \tfrac{1}{2}W\sqrt{\log M_r} + O(1),\ r \to \infty,$$

for an ascending divergent sequence $\{M_r\}$.

EXAMPLE 1 (B). *Suppose that*

$$M_1 = 2,\ M_r = M^2_{r-1}\ \textit{for}\ r \geqslant 2,$$

$$s_0 = s_1 = 0,\ s_n - s_{n-1} = -\frac{1}{2\sqrt{n}}\ \textit{for}\ 2 \leqslant n \neq M_r,\ r \geqslant 2,$$

$$s_{M_r} = \frac{\sqrt{\log M_r}}{2} \text{ i.e. } \begin{cases} s_{M_r} - s_{M_{r-1}} = \dfrac{\sqrt{\log M_r}}{2} + \sum\limits_{(\nu)} \dfrac{1}{2\sqrt{\nu}} = \dfrac{\sqrt{\log M_{r-1}}}{2} \\ M_{r-1} < \nu < M_r,\ r \geqslant 2. \end{cases}$$

Then

$$B(x) < O(1),\ x \to \infty.$$

Proof.—As in Example 2 (B), we shall suppose that r is taken after a stage, wherever necessary, in the inequalities which follow, and that $r \to \infty$ in the estimates deduced from them.

Case 1. $M_r \leqslant x \leqslant x_r = M_r + (\sqrt{\log M_r} - 2)\sqrt{M_r},\ r \to \infty.$

We write

$$B(x) \equiv \sum_0^\infty e^{-x} \frac{x^n}{n!}\ s_n = \Sigma_1 + \Sigma_2 + \Sigma_3 + \Sigma_4 + \Sigma_5 + \Sigma_6$$

where the range of variation of n in each of the sums Σ_r ($r = 1, 2, 3, \ldots, 6$) is as follows:

$$\Sigma_1\colon\ 0 \leqslant n \leqslant M_r - [\sqrt{(M_r \log M_r)}] - 1,$$

$$\Sigma_2\colon\ M_r - [\sqrt{(M_r \log M_r)}] \leqslant n \leqslant M_r - d_r - 1 \quad (d_r = [\sqrt{x_r}]),$$

$$\Sigma_3\colon\ M_r - d_r \leqslant n \leqslant M_r - 1,\ \ \Sigma_4\colon\ M_r \leqslant n \leqslant M_{r+1} - 1,$$

$$\Sigma_5\colon\ M_{r+1} \leqslant n \leqslant M_{r+2} - 1,\ \Sigma_6\colon\ M_{r+2} \leqslant n.$$

For the range of variation of n in Σ_1 we have

$$s_n = O(\sqrt{M_r}), \qquad \Sigma\, e^{-x} \frac{x^n}{n!} \leqslant \Sigma\, e^{-M_r} \frac{M_r{}^n}{n!} = O(1/\sqrt{M_r})$$

where the first estimate (for s_n) is obvious and the second estimate is obtained by Lemma II. Hence

$$\Sigma_1 = O(1).$$

Next $s_n < 0$ in Σ_2 and consequently

$$\Sigma_2 < 0.$$

Thirdly, for the range of variation of n in Σ_3,

$$s_n < -\frac{\sqrt{M_r}}{2},\ \sum e^{-x} \frac{x^n}{n!} \equiv \sum_{M_r - d_r}^{M_r - 1} e^{-x} \frac{x^n}{n!} > \frac{\{1 + o(1)\}}{\sqrt{(2\pi e)}} \frac{e^{\sqrt{\log M_r}}}{\sqrt{M_r}}$$

where the estimate for s_n is evident and the remaining estimate is the same as (6) of Example 2 (B). Hence

$$\Sigma_3 < -\text{ a positive constant. } e^{\sqrt{\log M_r}}.$$

Fourthly $s_n \leqslant \sqrt{\log M_r}/2$ in Σ_4 and so

$$\Sigma_4 < \frac{\sqrt{\log M_r}}{2}.$$

Next $|s_n| < \sqrt{n}$ in Σ_5 and therefore

$$\left|\Sigma_5\right| < \sum_{M_{r+1}}^{M_{r+2}-1} e^{-x}\frac{x^n}{n!}\sqrt{n} < 4\sum_{M_{r+1}}^{M_{r+2}-1} e^{-x}\frac{x^n}{n!}(\sqrt{n}-\sqrt{x})$$

since the last inequality is true for $x < M_{r+1}/2$ and *a fortiori* for $x \leqslant x_r$. Now we have

$$\sum_{1}^{\infty} e^{-x}\frac{x^n}{n!}\,|\sqrt{n}-\sqrt{x}| = O(1),\ x \to \infty, \tag{8}$$

by Lemma III with N chosen so that $N \leqslant x < N+1$. Hence

$$\Sigma_5 = O(1).$$

Finally we can treat Σ_6, in principle, like Σ_5 and prove that

$$|\Sigma_6| < \sum_{M_{r+2}}^{\infty} e^{-x}\frac{x^n}{n!}\sqrt{n} < 2\sum_{M_{r+2}}^{\infty} e^{-x}\frac{x^n}{n!}(\sqrt{n}-\sqrt{x}) = O(1)$$

provided only that $x < M_{r+1}$.

Case 2 (i). $x_r < x < M_{r+1}/2,\ r \to \infty$.

The estimates for Σ_1, Σ_2, Σ_5, Σ_6 in Case 1 continue to be valid; while the estimate for Σ_3 does not, since, in obtaining it, we have assumed (5) where it is supposed that $M_r \leqslant x \leqslant x_r$. However, it now suffices to observe that, for the range of variation of n in Σ_3, i.e. for $M_r - d_r \leqslant n \leqslant M_r - 1$, we have $s_n < 0$ and thus $\Sigma_3 < 0$.

The crudeness of the last estimate, $\Sigma_3 < 0$, is now compensated for by an estimate for Σ_4 which is more precise than the corresponding estimate in Case 1 and obtained as follows. For the range of variation of n in Σ_4, i.e. for $M_r \leqslant n \leqslant M_{r+1} - 1$,

$$s_n = s_{M_r} - \sum_{\nu=M_r+1}^{n}\frac{1}{2\sqrt{\nu}} = \frac{\sqrt{\log M_r}}{2} - \sqrt{n} + \sqrt{M_r} + o(1).$$

Therefore, since $x > x_r = M_r + (\sqrt{\log M_r} - 2)\sqrt{M_r}$, we get

$$s_n < \left(\frac{\sqrt{\log M_r}}{2} - \sqrt{x_r} + \sqrt{M_r}\right) + [\sqrt{x} - \sqrt{n} + o(1)], \tag{9}$$

$$\frac{\sqrt{\log M_r}}{2} - \sqrt{x_r} + \sqrt{M_r} = \frac{\sqrt{\log M_r}}{2} - \sqrt{M_r}\left(1 + \frac{\sqrt{\log M_r - 2}}{\sqrt{M_r}}\right)^{\frac{1}{2}} + \sqrt{M_r}$$

$$= 1 + o(1) < 2. \tag{10}$$

Substituting for s_n in Σ_4 the upper estimate following from (9) and (10), we find that

$$\Sigma_4 < 2 \sum_{M_r}^{M_{r+1}-1} e^{-x} \frac{x^n}{n!} + \sum_{M_r}^{M_{r+1}-1} e^{-x} \frac{x^n}{n!} \{\sqrt{x} - \sqrt{n} + o(1)\}$$

$$< 2 + O(1)$$

by (8).

Combining the last estimate for Σ_4 with the estimate $\Sigma_3 < 0$ and the estimates for Σ_1, Σ_2, Σ_5, Σ_6 in Case 1 which are still valid in the present case, we conclude as before that $B(x) < O(1)$, $x \to \infty$.

Case 2 (ii). $M_{r+1}/2 \leqslant x < M_{r+1}$, $r \to \infty$.

We now write

$$B(x) \equiv \sum_0^\infty e^{-x} \frac{x^n}{n!} s_n = \Sigma_1' + \Sigma_2' + \Sigma_3' + \Sigma_4' + \Sigma_5' + \Sigma_6'$$

where the range of variation for n in the component sums is as follows.

$$\Sigma_1' \colon 0 \leqslant n \leqslant [x] - [\sqrt{(x \log x)}] - 1,$$

$$\Sigma_2' \colon [x] - [\sqrt{(x \log x)}] \leqslant n \leqslant [x] - [\sqrt{x}] - 1,$$

$$\Sigma_3' \colon [x] - [\sqrt{x}] \leqslant n \leqslant [x] - 1, \quad \Sigma_4' \colon [x] \leqslant n \leqslant M_{r+1} - 1,$$

$$\Sigma_5' \colon M_{r+1} \leqslant n \leqslant M_{r+2} - 1, \quad \Sigma_6' \colon M_{r+2} \leqslant n.$$

As in Case 1, Lemma II with a slight modification gives

$$\Sigma_1' = O(1).$$

Also, since $s_n < 0$ in both Σ_2' and Σ_4', we have

$$\Sigma_2' < 0, \quad \Sigma_4' < 0.$$

Next

$$\Sigma_6' = O(1)$$

for the same reason that $\Sigma_6 = O(1)$ in Case 1.

Further, for the range of variation of n in Σ_3', we have

$$s_n < -\sqrt{(M_{r+1}/2)}/2$$

and, as in Case 2 of Example 2 (B),

$$\Sigma\, e^{-x}\frac{x^n}{n!} > [\sqrt{x}]\, e^{-x}\,\frac{x^{[x]-[\sqrt{x}]}}{([x]-[\sqrt{x}])!} = \frac{1+o(1)}{\sqrt{(2\pi e)}}$$

with the result that

$$\Sigma_3' < -\ \text{a positive constant.}\ \sqrt{M_{r+1}}.$$

Finally $s_n \leqslant \sqrt{\log M_{r+1}}/2$ in Σ_5' so that

$$\Sigma_5' < \frac{\sqrt{\log M_{r+1}}}{2}.$$

The estimates for Σ_r' $(r = 1, 2, \ldots .6)$ in the last five paragraphs together, with those for Σ_3' and Σ_5' combined, show that again $B(x) < O(1)$, $x \to \infty$.

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STUDIES IN THE FORMATION OF HETEROCYCLIC RINGS CONTAINING NITROGEN

Part I. Condensation of *o*-Phenylenediamine with Aromatic Aldehydes

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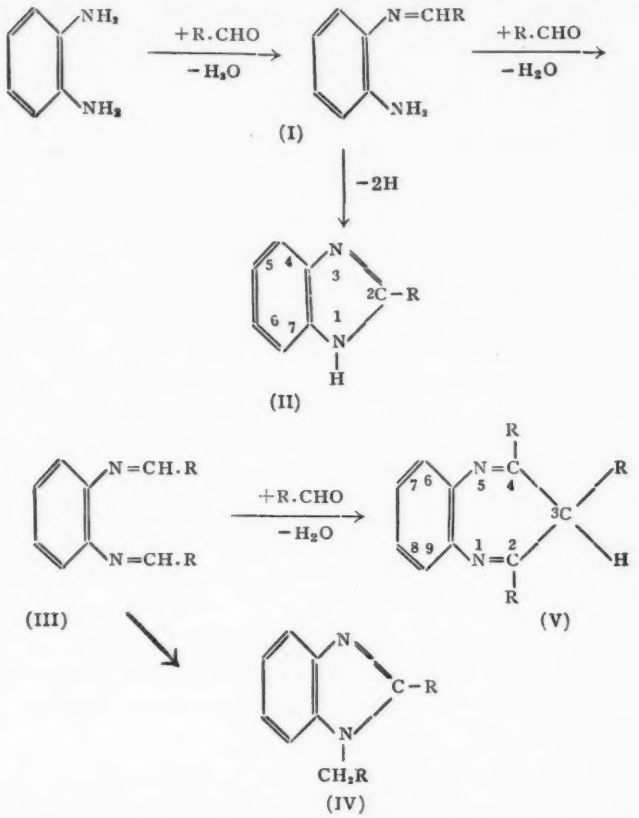
The reaction between *o*-phenylenediamine and aldehydes in the absence of any specific oxidising agent was first studied by Ladenburg and co-workers,[1, 2] and later extended by Hinsberg,[3] and Hinsberg and Funcke.[4] When one mole of the diamine was allowed to react with two moles of an aldehyde under acidic conditions, 'Aldehydines' or 1 : 2-disubstituted benziminazoles (IV), occasionally accompanied by 2-substituted benziminazoles (II), were found to be formed.

Both types of compounds were reported in the case of *m*- and *p*-nitrobenzaldehydes,[4, 5] whereas only compounds of type (IV) were obtained with benzaldehyde,[1, 6] *p*-hydroxybenzaldehyde,[7] vanillin,[6] anisaldehyde,[2, 7] and piperonal.[6] Salicylaldehyde was found to yield the dialdimine.[6, 7]

Weil and Marcinkowska[6] studied the reaction with three moles of benzaldehyde and isolated in addition to the disubstituted benziminazole, a compound of m.p. 159° C. to which benzodiazacycloheptatriene (V, R = Ph) structure was proposed.

During our studies on the ease and mode of formation of heterocyclic rings containing nitrogen, we had occasion to investigate the reaction between *o*-phenylenediamine and aromatic aldehydes without using any oxidising agent. Preliminary condensations with equimolecular proportions of the diamine and aldehydes indicated that only the disubstituted benziminazoles were formed predominantly. Therefore, in subsequent experiments, two moles of the aldehyde have been used throughout. The results obtained by the condensation with eighteen aromatic aldehydes, inclusive of those already reported by us,[8] are summarised in Table I. The isolation of 2-substituted benziminazoles, formed in small quantities along with the disubstituted compounds, was made possible by modifying the experimental procedure of Hinsberg.[3]

The reaction of *o*-phenylenediamine with an aldehyde R.CHO in glacial acetic acid medium forming compounds of types (II), (IV) and (V), appears to proceed through the following steps:



Since two molecular proportions of aldehyde have been used in the condensation, it is but natural to expect the formation of (IV) as major product, and the other two compounds, (II) and (V), if formed, as minor products.

In general, neither the monoanil (I), nor the dianil (III) could be isolated under the normal reaction conditions. This is perhaps due to these unsaturated intermediates readily undergoing cyclisation or further condensation with the aldehyde resulting in the formation of final products. However, during these studies, isolation of a compound in the condensation with salicylaldehyde identical with the dianil reported earlier,[6, 7] when the reaction has been carried out under controlled conditions using minimum amount of solvent, supports the suggested course of the reaction.

Exclusive formation of disubstituted benziminazoles from the three isomeric hydroxybenzaldehydes, vanillin, and *p*-dimethylamino-benzaldehyde,

shows that electron-releasing groups like hydroxy or amino as substituents in the aldehydes facilitate the reaction leading to the formation of (IV) almost quantitatively.

TABLE I

Products of condensation of o-phenylenediamine with aldehyde R.CHO

No.	R-	Percentage yield of 1 : 2-Disubstituted benziminazole (IV)	2-Substituted benziminazole (II)	Benzodiazacyclo-heptatriene (V)
1	Ph-	63	23	2
2	*o*-OH.C_6H_4- ..	82*	..	..
3	*m*-OH.C_6H_4- ..	95*	..	..
4	*p*-OH.C_6H_4- ..	95	..	..
5	*m*-MeO.*p*-OH.C_6H_3..	95	..	..
6	*p*-MeO.C_6H_4- ..	64	18	..
7	3 : 4-(CH_2O_2).C_6H_3- ..	75	23	..
8	*o*-Cl.C_6H_3- ..	68*	31	..
9	*p*-Cl.C_6H_4-.. ..	68*	24	..
10	2 : 4-$(Cl)_2$.C_6H_3- ..	..	50	..
11	3 : 4-$(Cl)_2$.C_6H- ..	76*	6*	..
12	*p*-Br.C_6H_4-.. ..	82*	15	..
13	*o*-NO_2 C_6H_4- ..	11*	50	..
14	*m*-NO_2 C_6H_4- ..	70	8	10*
15	*p*-NO_2.C_6H_4- ..	59	26	..
16	*m*-NO_2.*p*-OH.C_6H_3-	69*	20*	..
17	*p*-N $(Me)_2$.C_6H_4- ..	97*	..	..
18	*l*-$C_{10}H_7$-	70*	20	..

* Compounds not so far reported in literature.

The monosubstituted benziminazoles (II) could be isolated, although in comparatively smaller proportion, along with the disubstituted compounds, in the condensation with twelve aldehydes (see Table I). 2 : 4-Dichlorobenzaldehyde, however, gave exclusively type (II) compound. The formation of this type of product by the oxidative cyclisation of the monoanil (I) has been established by the extensive researches of Fischer,[9] Boyd,[10] Hinsberg and collaborators,[4, 11] Jacobson, Jaenicke, and Meyer,[12] Stephens and Bower,[13] and Jerchel and co-workers.[14] Such oxidative cyclisation in the present reaction may be taking place due to the action of air as reported by earlier workers, or by the action of the aldehyde which is present in the reaction mixture.

Among the thirteen aldehydes giving rise to this type (II) product, the nitro- and halo-substituted ones in general, yielded a fairly good quantity of this compound. Perhaps, these electron-attracting substituents considerably facilitate the oxidative cyclisation of the monoanil resulting in higher yields of monosubstituted benziminazoles.

In the case of benzaldehyde and *m*-nitrobenzaldehyde reactions, in addition to the mono- and disubstituted benziminazoles, compounds of type (V) could be isolated. The formation of these products may be explained on the basis of further condensation of the dianil (III) with another mole of the aldehyde. Although the structure assigned appears to be possible from the analytical data obtained, it requires further confirmation either by degradative methods or by a study of their physico-chemical properties. Further work in this direction is in progress.

Since many of the substituted benziminazoles have been reported in literature to be highly physiologically active, particularly possessing antibacterial and antifungal properties, some of the compounds isolated during this investigation have been tested against bacteria, fungi, and also fish, and found to be appreciably active. Details of their physiological activity will be reported later.

EXPERIMENTAL

All m.p.'s are uncorrected. The microanalyses were carried out by one of the authors (C. V. R.) in our Micro-Analytical Laboratories.

General procedure for the condensation of o-*phenylenediamine with aromatic aldehydes*:

Hinsberg's procedure for the condensation was modified as follows : *o*-Phenylenediamine (one mole) and aromatic aldehyde (two moles) were dissolved separately in a slight excess of glacial acetic acid, and mixed together in a conical flask, when evolution of heat was observed. The reaction was allowed to proceed at room temparature for one hour with occasional stirring. Then the reaction mixture was filtered if any solid separated at this stage, and the clear solution poured into large amount of crushed ice with vigorous stirring. The solid that separated was filtered, and the filtrate made ammoniacal, when a small amount of another solid was obtained. The products thus obtained were purified and characterised.

In the case of *p*-dimethylaminobenzaldehyde, however, the condensation did not proceed at room temparature, and therefore, the reaction was conducted at 100° C. for four hours to give the best results.

Products of condensation:

The solids that separated out from glacial acetic acid in the condensations with benzaldehyde and *m*-nitrobenzaldehyde were characterised as benzodiazacycloheptatriene derivatives (V), whereas the compounds obtained by the addition of crushed ice to the acid solution were found to be the disubstituted benziminazoles, and those obtained from ammoniacal solution, the monosubstituted compounds.

In the case of the ten aldehydes wherein both mono- and disubstituted benziminazoles were isolated, in general, the products obtained from aqueous acetic acid solution were the disubstituted compounds, while those from ammoniacal solution were found to be the monosubstituted products. However, the following three minor exceptions were observed:

(1) In the *o*-nitrobenzaldehyde condensation, a low melting solid which appeared to be a mixture was obtained from dilute acid solution. This mass was treated with moderate quantity of benzene, when a relatively high proportion of a granular solid separated out. The solid was filtered, and the filtrate on concentration gave a resinous mass. The granular solid on recrystallisation gave a pure compound, m.p. 261° C., found to be identical with the monosubstituted benziminazole. The resinous mass yielded a pure crystalline product of m.p. 120° C., on repeated crystallisations from ethyl alcohol, and this was characterised as the disubstituted compound. The product from ammoniacal solution, m.p. 261° C., was identified as the pure monosubstituted benziminazole.

(2) A crystalline solid melting above 300° C., that separated from glacial acetic acid in *p*-nitrobenzaldehyde condensation, on careful scrutiny was found to be identical with the anhydrous form of monosubstituted compound reported earlier.[4, 15] The product obtained by the addition of crushed ice to the clear acid solution was identified as the disubstituted benziminazole of m.p. 212° C., and that from ammoniacal solution, m.p. 298° C., as the sesquihydrate of monosubstituted compound.[16]

(3) In the case of *m*-nitro-*p*-hydroxybenzaldehyde condensation, a substance melting above 300° C., could be isolated from the dilute acid filtrate only by making the latter just neutral with ammonia, since the product formed was found to be soluble in excess of acid as well as alkali. This analysed for the monosubstituted benziminazole.

From salicylaldehyde and *m*-hydroxybenzaldehyde reactions, the compounds obtained from dilute acid solution in larger proportion, and from ammoniacal solution in smaller amounts, were found to be the same, and

were identified as the disubstituted benziminazoles. But, in the condensations of *p*-hydroxybenzaldehyde, vanillin, and *p*-dimethylamino benzaldehyde, practically no solid separated out on the addition of the acetic acid solution to crushed ice, and the products obtained on making the acid solution ammoniacal were found to be the disubstituted compounds.

TABLE II

Properties and analytical data of the new compounds

No.	Aldehyde condensed	Name of the compound	Colour
1	Benzaldehyde ..	2 : 3: 4-triphenyl benzodiazacycloheptatriene[b,c]	colourless
2	Salicylaldehyde ..	1-(*o*-hydroxybenzyl)-2-(*o*-hydroxyphenyl)-benziminazole	colourless
3	*m*-Hydroxybenzaldehyde	1-(*m*-hydroxybenzyl)-2-(*m*-hydroxyphenyl)-benziminazole[f]	colourless
4	*o*-Chlorobenzaldehyde ..	1-(*o*-chlorobenzyl)-2-(*o*-chlorophenyl) benziminazole	pale yellow
5	*p*-Chlorobenzaldehyde ..	1-(*p*-chlorobenzyl)-2-(*p*-chlorophenyl)-benziminazole[d]	pale yellow
6	3: 4-Dichlorobenzaldehyde	1-(3:4-dichlorobenzyl)-2-(3:4-dichlorophenyl)-benziminazole[e]	colourless
7	do	2-(3 : 4-dichlorophenyl)-benziminazole[f]	colourless
8	*p*-Bromobenzaldehyde ..	1-(*p*-bromobenzyl)-2-(*p*-bromophenyl)-benziminazole	colourless
9	*o*-Nitrobenzaldehyde ..	1-(*o*-nitrobenzyl)-2-(*o*-nitrophenyl)-benziminazole	yellow
10	*m*-Nitrobenzaldehyde ..	2: 3: 4-tri-(*m*-nitrophenyl)-benzodiazacycloheptatriene[c]	brown
11	*m*-Nitro-*p*-hydroxy-benzaldehyde	1-(*m*-nitro-*p*-hydroxybenzyl) 2-(*m*-nitro-*p*-hydroxypheny)-benziminazole[c]	lemon yellow
12	do	2-(*m*-nitro-*p*-hydroxyphenyl) benziminazole[g]	bright yellow
13	*p*-Dimethylamino-benzaldehyde	1-(*p*-dimethylaminobenzyl)-2-(*p*-dimethylaminophenyl)-benziminazole[f]	colourless
14	1-Naphthaldehyde ..	1-(1-naphthyl) methyl-2-(1-naphthyl)-benzim nazole[f]	colourless

(*a*) Unless otherwise stated, compounds are recrystallised from ethyl alcohol containing appropriate quantity of water.

(*b*) Although this compound has been reported by Weil and Marcinkowska (*ref.* 6), the properties of the compound are presented as it is of a new type.

(*c*) These compounds are recrystallised from a mixture of ethyl alcohol and acetone.

(*d*) Before recrystallisation, the compound is freed from a little accompanying resin by washing with petroleum ether (b.p. 40–60° C.).

(*e*) A small amount of resinous mass accompanying the compound is removed before recrystallisation by treatment with a little quantity of methanol.

(*f*) The recrystallisation of these compounds has been effected with benzene.

(*g*) The compound is recrystallised from ethyl acetate.

In the 2 : 4-dichlorobenzaldehyde reaction, a low melting solid was obtained from the aqueous acid solution. This on treatment with a small quantity of ethyl acetate, yielded a granular substance, which on recrystallisation gave a crystalline product, m.p. 227° C., identified as the monosubstituted benziminazole. The small amount of substance that could be isolated from the ammoniacal solution was also found to be identical with the monosubstituted compound.

Crystalline shape	m.p. in °C.	Formula	Found %			Required %		
			C	H	N	C	H	N
needles	159	$C_{27}H_{20}N_2$	87·0	5·6	7·8	87·1	5·4	7·5
rectangular plates	220	$C_{20}H_{16}N_2O_2$	75·9	5·3	8·6	76·0	5·1	8·9
rectangular rods	250	$C_{20}H_{16}N_2O_2$	75·9	5·2	8·9	76·0	5·1	8·9
rectangular prisms	159	$C_{20}H_{14}N_2Cl_2$	67·8	4·1	7·9	68·0	4·0	7·9
prismatic needles	136	$C_{20}H_{14}N_2Cl_2$	67·6	4·1	8·2	68·0	4·0	7·9
needles	146	$C_{20}H_{12}N_2Cl_4$	56·5	3·2	6·6	56·9	2·8	6·6
rhombic prisms	229	$C_{13}H_8N_2Cl_2$	59·6	3·3	10·8	59·3	3·0	10·6
needles	158	$C_{20}H_{14}N_2Br_2$	53·9	3·4	6·2	54·3	3·2	6·3
needles	120	$C_{20}H_{14}N_4O_4$	64·0	4·1	14·9	64·2	3·7	15·0
needles	195	$C_{27}H_{17}N_5O_6$	63·5	4·0	13·8	63·9	3·4	13·8
plates	226 (decomp.)	$C_{20}H_{14}N_4O_6$	59·6	3·7	13·6	59·1	3·5	13·8
needles	>300	$C_{13}H_9N_3O_3$	61·5	3·9	16·3	61·2	3·5	16·5
rectangular rods	255	$C_{24}H_{26}N_4$	77·8	7·4	15·4	77·8	7·0	15·1
needles	160	$C_{28}H_{20}N_2$	87·2	5·6	7·2	87·5	5·2	7·3

The analytical data and properties of the new compounds isolated during this investigation are given in Table II.

Summary

The reaction between *o*-phenylenediamine and eighteen aromatic aldehydes under acidic conditions has been investigated, and found to yield mono- and disubstituted benziminazoles in varying proportions, and in two cases, a benzodiazacycloheptatriene derivative also. Thirteen new compounds obtained have been characterised. Stepwise mechanism for the formation

of the different types of products is suggested, and the influence of substituents in the aldehydes on the mode of the reaction and cyclisation is discussed.

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NUCLEAR DISINTEGRATIONS PRODUCED IN NUCLEAR EMULSIONS BY α-PARTICLES OF GREAT ENERGY

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Abstract

A study of nuclear disintegrations caused by α-particles of primary cosmic radiation with energies > 5 BeV per nucleon, has been carried out. In a systematic survey in nuclear emulsions using 'along the track' scanning method, 479 α-particles with a total track length of 40·84 metres and 242 interactions were obtained. From the angular distribution of shower particles associated with these interactions, a procedure has been found for distinguishing protons, which originally formed part of the incident α-particle and which have not taken part in the interaction, from other charged particles. The mean free path for nuclear interaction in G-5 emulsion is found to be $17{\cdot}5 \pm 1{\cdot}1$ cm. ($68{\cdot}9 \pm 4{\cdot}3$ gm./cm.^{2}). Assigning both to the incident α-particle and to the target nuclei a radius $R = r_0 A^{\frac{1}{3}}$, one obtains an effective nuclear radius $r_0 = 1{\cdot}13 \pm 0{\cdot}04 \times 10^{-13}$ cm. Using the number of protons emerging from disintegrations of heavy nuclei (Silver and Bromine) without having participated in the interaction (as can be deduced from the angular distribution) and assuming spherical nuclei of uniform density, the mean free path of nucleons in nuclear matter is calculated to be less than $3{\cdot}2 \times 10^{-13}$ cm.

1. Introduction

For the study of nuclear reactions above 6 BeV, only cosmic ray particles are available at present. Such interactions can be observed in emulsions exposed in the stratosphere. The great majority of such interactions is produced by singly charged particles, but in general it is not possible to say in those interactions, whether the incident particle is of primary or secondary origin. Therefore, even if the exposure is made at low latitudes, one cannot easily separate interactions of particles of energy above several BeV from those of lower energy. This separation is, however, possible if one confines oneself to primary α-particles. In this case at a given latitude, one deals

with known particles with a known energy spectrum and fairly well-defined minimum energy. On the other hand, one has to accept the disadvantage of dealing with collisions whose interpretation is more complex than those initiated by singly charged particles. Still, in the interest of obtaining an uncontaminated sample of high energy interactions we have thought it worth while to study the nuclear processes in emulsions due to α-particles whose energy exceeds 5 BeV/nucleon.

Apart from obtaining a mean free path for various types of interactions, it turns out that one can separate in these interactions, the protons which originally formed part of the incident α-particle and which have not collided with any part of the target nucleus, from the remaining shower particles, namely, protons which have interacted, and charged mesons which have been produced in the collision. This separation which is based on the angular distribution of shower particles may, in the future, be of use in the study of high energy interactions, because it permits the identification in the shower core of tracks of singly charged particles whose energy is known to be close to the energy per nucleon of the primary.

Nuclear interactions caused by artificially produced α-particles with energies upto about 100 MeV per nucleon have been studied by various worker.[1, 2] A few investigations have also been carried out using α-particles from the cosmic radiation.[3–5] In the latter experiments, the emulsions were exposed to the cosmic radiation at latitudes where the geomagnetic cut off for α-particles was less than 500 MeV/nucleon. Our work differs from that of other investigators using α-particles of cosmic radiation, in that we obtained an appreciably larger number of interactions and worked with α-particles whose lower energy limit was 5 BeV/nucleon. In order to compare the characteristics of interactions produced by these α-particles directly with those produced by protons of comparable energy we also obtained stars produced by 6·2 BeV protons of the Berkeley Bevatron.*

2. EXPERIMENTAL PROCEDURE AND RESULTS

In order to obtain an unbiased selection of interactions produced by high energy α-particles as well as by 6·2 BeV protons of the Berkeley Bevatron, we adopted the 'along the track' method where the track of the primary particle is first observed and then followed until it makes an interaction or leaves the emulsion stack.

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* We are grateful to Professor Leprince-Ringuet of the Ecole Polytechnique, Paris, for kindly lending us two of their emulsions exposed to the direct beam of the Berkeley Bevatron.

2.1. Emulsion Blocks Used for Obtaining the α-Particle Interactions

The experiment was carried out almost exclusively with one emulsion block consisting of 200 G-5 emulsions, 600 μ thick and of size 15 × 15 cm. This stack was flown from Delhi and it floated above an altitude of 70,000 ft., for about 3 hours. The geomagnetic cut off for α-particles at Delhi (19° N.) is 5·3 BeV/nucleon. About 10% of the interactions came from a second stack flown from Ahmedabad (13° N. and 5·8 BeV/nucleon geomagnetic cut off) at a mean altitude of 60,000 ft. for 3½ hours.

In both these exposures, the geomagnetic cut off is so high that all primary α-particles have four times the ionization of relativistic singly charged particles. In our emulsions this corresponds to about 3·5 times the grain density at the plateau of ionization for singly charged particles.

2.2. Selection of Tracks

We scanned the plates under a total magnification of × 375 and selected tracks which fulfilled the following criteria :

(*a*) The grain density by visual judgment was in the neighbourhood of 3·5 times the plateau value for singly charged particles ;

(*b*) The track length per emulsion was $\geqslant$ 5 mm. ;

(*c*) The potential range in the stack was $\geqslant$ 5 cm.

These tracks should have been produced either by relativistic α-particles or by slow singly charged particles—protons, deuterons or tritons. In order to differentiate between relativistic α-particles and slow protons, deuterons and tritons a rough estimate of the coulomb scattering of these particles was made in the following manner :

The hairline in the microscope eye-piece was set exactly along the track and it was followed from its point of entrance to that of exit in the emulsion. It can easily be seen that if by error of visual judgment we included even a triton of grain density as low as 3·0 times the plateau value, its deviation due to coulomb scattering in a distance of 5 mm. is quite appreciable ($\sim 5\mu$) and can be detected visually under the maginification of × 375 that we employed. In some cases where it was not possible to decide with certainty in the first emulsion, a similar test in the succeeding one was sufficient to separate relativistic α-particles from slow protons, deuterons and tritons. We would like to point out here that these emulsions after processing had small distortions ($\leqslant$ 20 covans).

That the above test was sufficient to identify relativistic α-particles can also be seen in the following way. Every track must have a minimum

TABLE I

Size frequency distribution of α-induced interactions

N_4 / N_7	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	⩾25	Total
0																											0
1			1																								1
2	16	6	1	2	1	1	1																				28
3	5	2	2		1																						10
4	2	3		2	1					1						1											10
5	5	2	2	5	1		2	1	1		1		1											1			22
6	4		2	2	2	2										1											13
7	2					1	1			1	1		1				1				1					1	10
8		1	1	1	1		3	1			2	1				1		1								1	14
9	1	1			3			1						1													7
10				2	4	3	1			1				1		1								1		1	15
11	2	1		4	1	5			1		2·	2	1		1		1					1				1	23
12											1			1	1			1								3	7
13			1			1											2		1		1			1	3	1	8
14			1		1	1	1		2			1										1					8
15						1							1	1						1				3	1		8
16									2				1			1			1								5
17																	1	1								1	3
18			1	1												1					1						4
19																								1	1	1	3
⩾20		1	1			1						1		3	1			1		2	1	1		3		3	19
Total	37	17	13	19	16	16	9	3	6	3	7	5	5	7	3	6	5	4	2	3	4	3	0	10	2	13	218

α in–α out interactions

| 0 | | 7 | | 1 | 2 | | |

potential range of 5 cm. in order to satisfy our selection criteria; a triton of grain density as low as 3·0 times the plateau value should show a significant and easily recognizable increase in grain density in this distance, yet none of the tracks selected showed an observable change of grain density along the entire track length. If the selected track terminated in a star, it was always a high energy star with relativistic prongs, a type of star which cannot be produced by a slow proton, deuteron or triton. Thus, from all these considerations we feel that we have obtained a selection of primary α-particle tracks without contamination from slow singly charged particles. A further argument in favour of this conclusion will be given in 4.1.

2.3. THE RESULTS

We have selected a total of 479 α-particle tracks with a total track length of 40·84 metres and obtained 242 interactions. For the 6·2 BeV protons we obtained a total track length of 35·69 metres and 103 interactions. We would like to point out here that the median energy of the α-particles is about 10 BeV/nucleon, whereas the proton energy is only 6·2 BeV, this being the highest energy available at present from accelerators.

The interactions produced by α-particles could be classified in the first instance into two types:

(*a*) Events in which a relativistic doubly charged particle continues almost along the same direction as the primary α-particle (α in-α out events);

(*b*) Interactions in which only singly charged relativistic particles and other non-relativistic particles are emitted (α-destructive collisions).

Various types of interactions produced by α-particles are illustrated in Fig. 1.

The distribution of the 242 interactions according to the number of shower particles n_s and the number of heavily ionizing particles N_h is shown in Table I.

3. CLASSIFICATION OF THE INTERACTIONS ACCORDING TO THE NUMBER OF PROTONS TAKING PART IN THE COLLISION PROCESS

A visual examination of all the (0+2) α events† strongly indicated that the relativistic singly charged particles emerging from these collisions either

† In accordance with the nomenclature introduced by Brown *et al.*,[6] the first number designates the number of grey or black tracks (N_h), the second number designates the number of charged shower particles, *i.e.*, tracks whose ionization is less than 1·5 times that produced by singly charged relativistic particles. The symbol outside the brackets indicates the nature of the primary particle initiating the collision.

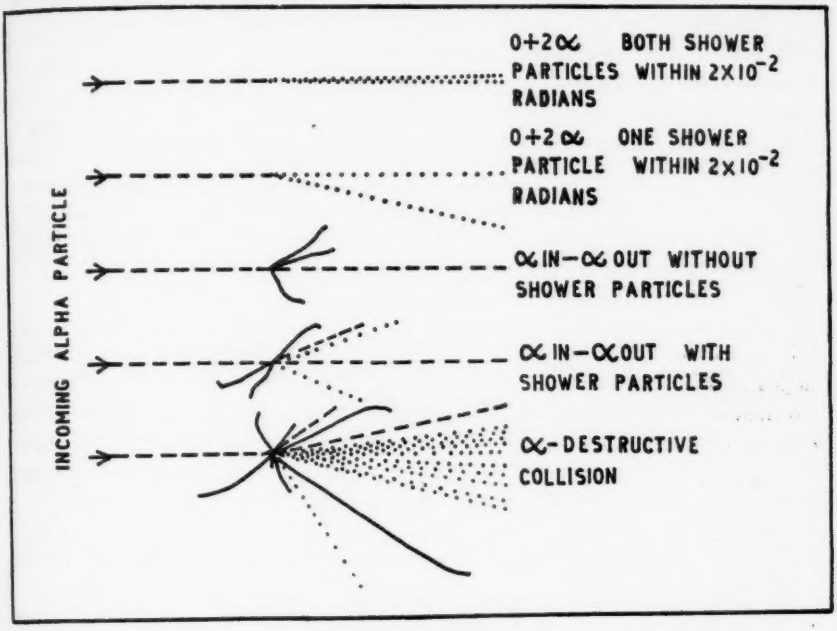
INCOMING ALPHA PARTICLE
0+2∝ BOTH SHOWER PARTICLES WITHIN 2X10⁻² RADIANS
0+2∝ ONE SHOWER PARTICLE WITHIN 2X10⁻² RADIANS
∝IN-∝OUT WITHOUT SHOWER PARTICLES
∝IN-∝OUT WITH SHOWER PARTICLES
∝-DESTRUCTIVE COLLISION

FIG. 1. Figure showing typical examples of interactions caused by α-particles of energy ⩾5 BeV/nucleon in nuclear emulsions.

continue almost in the same direction as the primary or make fairly large angles with it. This observation suggests that if accurate angular measurements are made on the shower particles of all the disintegrations it might be possible to separate in individual interactions the protons that have not taken part in the collisions from those which have.

3.1. The Angular Distribution of the Shower Particles

Angular measurements were made on those events where:

(*a*) The primary α-particle and also the shower particles in the forward direction had at least 1 mm. track length in the same emulsion;

(*b*) The event was situated in a region of the emulsion far away from the processed edge (⩾ 1 cm.) and free from bubbles;

(*c*) The energy involved in the disintegration estimated from the opening angle of the shower (for $n_s \geqslant 10$) was ⩽ 50 BeV/nucleon.

A total of 176 interactions which satisfied the above conditions was obtained. Tracks which made angles greater than 10^{-1} radian were measured by determining the projected angles and the dip angles under a total magnification of $\times 675$ (using $\times 45$ oil immersion). Only $150\,\mu$ track length was used in these measurements. Tracks making angles less than 10^{-1} radians were measured in the following manner:

The α-particle track was aligned along the x-axis on a scattering microscope and the y-coordinate of the track was measured every $200\,\mu$ for a distance of $\geqslant 1$ mm. This was done in the same setting for each secondary particle which made a projected angle of $\leqslant 10^{-1}$ radians. Depth measurements were also made every $200\,\mu$ using at least 1 mm. length of the primary track and the same length for each secondary. By this method the projected angles could be measured accurately to 5×10^{-4} radians, while the depth measurements were accurate to 5×10^{-3} radians. Therefore, the errors in our measurements of angles $\leqslant 10^{-1}$ radians will be of order 5×10^{-3} radians.

In Fig. 2 (*a*) we give the angular distribution of shower particles below 10^{-1} radians. We have also included in this figure the doubly charged par-

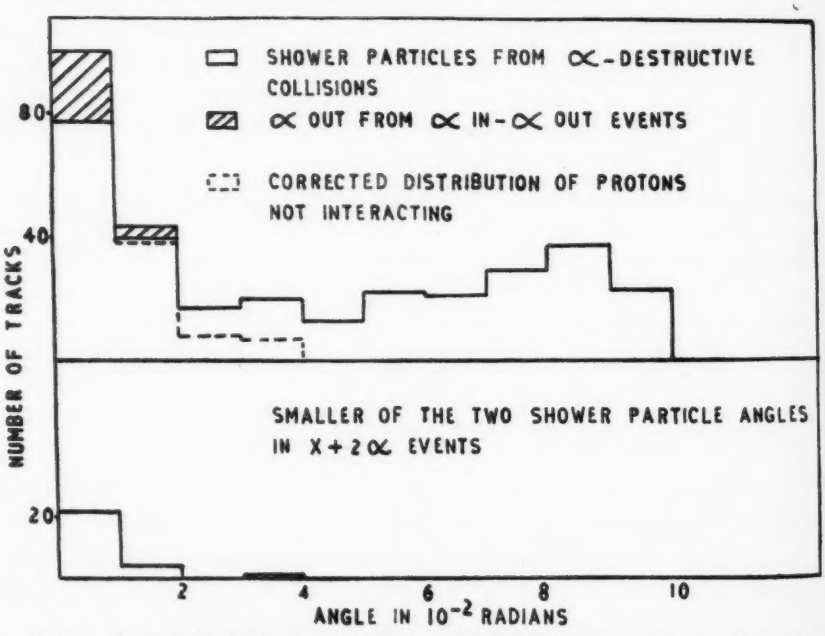

FIG. 2. (*a*) Angular distribution of shower particles ejected at angles less than 10^{-1} radians from α-particle induced interactions.

(*b*) Angular distribution of shower particles which make the smaller of the two angles with the primary in events of the type $(x + 2)\,\alpha$.

ticles (counting each as equivalent to 2 shower particles) emerging from α in–α out events; the corresponding part of the histogram has been shaded.

It is seen from Fig. 2 (*a*) that there is a narrow peak at $0\text{–}2\times10^{-2}$ radians and an apparently significant trough in the distribution at an angle of about 4×10^{-2} radians.

3.2. Separation of Protons that have not Taken Part in Inter-Actions from the Rest of the Shower Particles

The shower particles associated with the α-disintegrations are due either to:

(*a*) Protons which formed part of the incident α-particle and have not taken part in nuclear interaction with the target nucleus;

(*b*) 'Secondary shower particles' defined as protons that have made nuclear interactions, fast recoil protons and mesons produced in the collision.

We will now present evidence that the trough in the angular distribution [Fig. 2 (*a*)] arises from the fact that almost all particles (*a*) are emitted at angles smaller than 2×10^{-2} radians, while particles (*b*) are very rarely emitted within this angle.

(*i*) In Fig. 3 we give the track density per unit solid angle for the interval of $0\text{–}10^{-1}$ radians.

It is seen that in the interval of 5×10^{-2} to 10^{-1} radians the track density is constant within experimental errors. The mean track density in this angular interval is found to be $5{\cdot}60 \pm 0{\cdot}50 \times 10^3$ particles per steradian. This distribution strongly indicates that the narrow peak between $0\text{–}2\times10^{-2}$ radians is due to a process which differs from that which gives rise to the majority of shower particles. Presumably it is due to protons which have not themselves collided with nucleons in the target. If we make the reasonable assumption that the secondary shower particle density has the same value from $0\text{–}5\times10^{-2}$ radians as it has from 5×10^{-2} to 10^{-1} radians, we can separate the protons that have not interacted from other particles. The density distribution of protons which passed through the target without interacting is shown by a dotted line in Fig. 3. We now define a cut off angle which contains 90% of the protons that have not participated in collision processes. This angle is found to be 2×10^{-2} radians. A cut off angle of 2×10^{-2} radians is chosen because the contribution of 'secondary shower particles' within this angle is very small (about 5% of the particles within the cut off angle are 'secondary shower particles') and, therefore, allows

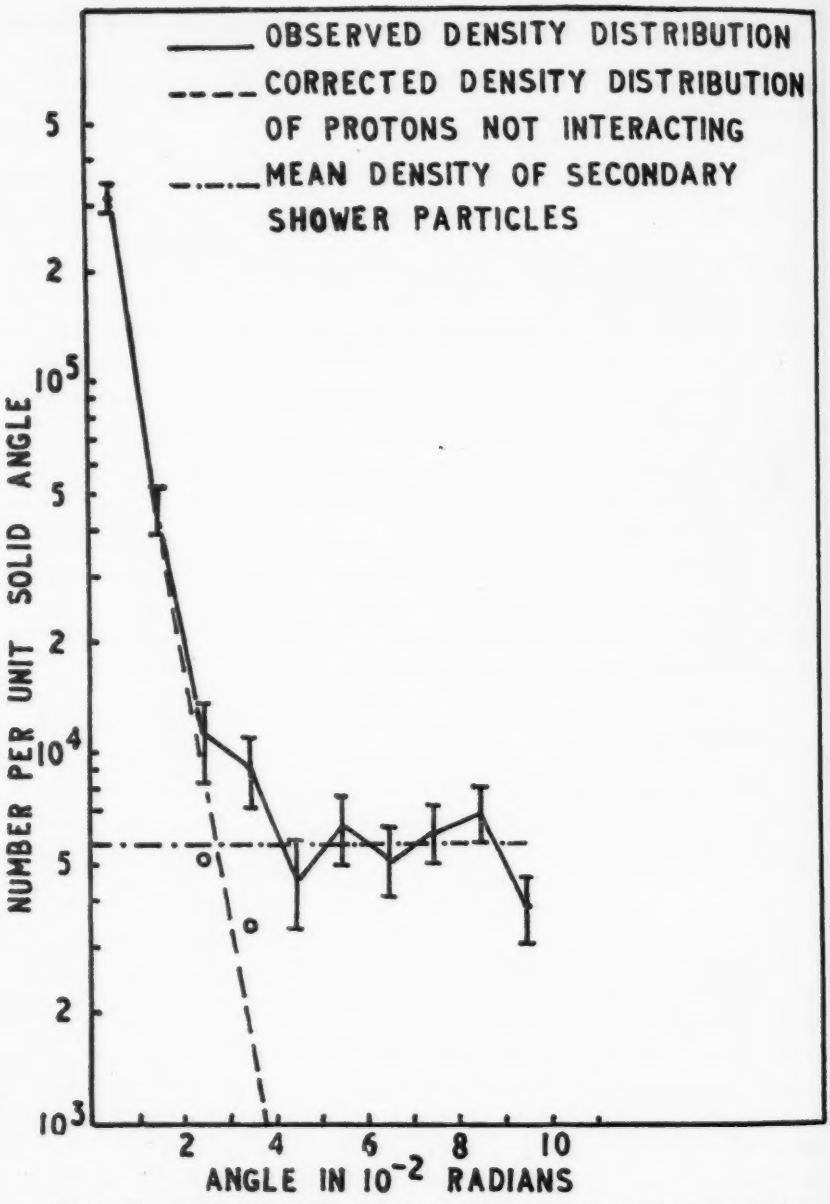

FIG. 3. The experimental points show the density per steradian of shower particles associated with interactions produced by 3-particles. The mean density of 'secondary shower particles' is shown thus —·---·— in the figure.

The dashed line represents the corrected density distribution for protons that have not made any collisions in the target nucleus.

identification *in individual events* of protons that have not participated in collisions, without much ambiguity. The remaining evidence (*ii–vi*) is in good agreement with this conclusion.

(*ii*) In events of the type $(x+2)$ α the two shower particles are presumably in almost all cases the same two protons which originally were bound in the incident α-particle. Except for a few events which result from coulomb interaction (see 3.3), it is reasonable to assume that only one nucleon takes part in this type of interaction, because the chance of two interacting and still not producing any charged meson should be very small at energies above 5 BeV/nucleon. If this is so, then in all 26 events of this type there should be at least one proton which has not interacted, and at least one of the two shower particles should then make an angle less than 2×10^{-2} radians with the primary. In Fig. 2 (*b*) we have plotted for all $(x+2)$ α events the angular distribution of those shower particles which make the smaller of the two angles with the primary. The histogram shows that in 25 of the 26 events at least one track makes an angle of less than 2×10^{-2} radians with the primary. In the 26th case the smaller of the two angles is $3{\cdot}5\times10^{-2}$ radians. It is found that 75% of the shower particles in the $(x+2)$ α events fall within the angular interval $0\text{–}2\times10^{-2}$ radians (only 11% of the shower particles from all measured events fall into the same angular interval).

(*iii*) If, now we consider only events of high multiplicity (irrespective of other considerations), then in most cases both protons belonging to the primary α-particle should have made collisions and, therefore, should emerge outside the cut off angle. Therefore, we selected stars with $n_s \geqslant 20$ and found that out of 205 shower particles associated with nine interactions, only two are ejected at angles less than 2×10^{-2} radians. Less than 1% of the shower particles in this type of events fall within the cut off angle 2×10^{-2} radians.

The relatively small proportion of shower particles emitted within the cut off angle in interactions of high multiplicity and the very large proportion of such particles associated with interactions of the type $(x+2)$ α (stars where no charged meson is produced) strongly favour our hypothesis.

(*iv*) It will be shown in 3.3 that in each α in–α out event only one neutron should have participated in the collision, therefore, all shower particles associated with them should necessarily be secondary in nature and fall outside the cut off angle. There are 15 shower particles in this type of events and none of them falls within the interval $0\text{–}2\times10^{-2}$ radians.

(*v*) We have also studied the angular distribution of shower particles from stars produced by 6·2 BeV protons. Here we know that all shower

particles should be 'secondary' in nature (type *b*). We find that out of a total of 258 shower particles associated with 99 of these stars, only one is emitted at an angle less than 2×10^{-2} radians.

(*vi*) Another indirect evidence for the validity of choosing a cut off angle of 2×10^{-2} radians is offered from the size distribution of events when classified according to the number of interacting protons (obtained by using this cut off angle to separate protons that have not interacted, from the rest). It is found (Table II) that the mean number of shower particles $< n_s >$ and the mean number of heavy prongs $< N_h >$ increase as the number of interacting protons increases.

The evidence given above proves the correctness in our procedure of separating protons that have not interacted from the rest of the shower particles. It is seen from Fig. 3 that the corrected total number of protons that have not participated in collisions should be 151. From Fig. 2 (*a*), we see that there are 143 particles observed within the cut off angle. From the angular distribution given in Fig. 3, and the definition of the cut off angle given earlier in this section, it follows that the 143 particles observed within 2×10^{-2} radians should contain 136 protons that have not interacted as well as 7 'secondary shower particles'. Thus, it becomes possible to separate without much ambiguity in individual interactions, protons that have not participated in collisions from those which have.

Singly charged relativistic particles emitted within the cut off angle are almost always fragments of the incident α-particle and we have so far simply designated them as protons. Actually they may emerge as protons, deuterons or tritons. In the experiment carried out by Quareni and Zorn,[1] with 90 MeV/nucleon α-particles, events were observed where an incident particle just split into two singly charged particles of the same velocity as the α-particle. Among these secondary particles they were able to identify protons, deuterons and tritons. It is, therefore, likely that in our events also, there are protons, deuterons and tritons emitted at angles less than 2×10^{-2} radians. This observation will not affect our subsequent analysis since we will consider complete symmetry in behaviour between protons and neutrons as far as the nuclear interactions are concerned.

3.3. (0 + 2) α AND α IN–α OUT EVENTS

Among the events on which accurate angular measurements were possible there are 11 examples of (0 + 2) α type in which both outgoing particles are contained within an angle of 2×10^{-2} radians and 9 examples of α in–α out [$(x + 0 + \alpha)$ α] without any associated shower particle. These events could arise from either:

(*a*) Interactions in which only neutrons are involved and no charged mesons are produced; or

(*b*) The disintegration of the α-particles in the coulomb field of the target nucleus (0 + 2) α; or

(*c*) The break up of the target nucleus in the coulomb field of the α-particle (α in–α out).

In order to estimate the proportion of (0 + 2) α and α in–α out events arising from coulomb interactions, we made use of the treatment employed by Weizsacker to calculate the frequency spectrum of virtual photons associated with a charged particle in motion. Using the virtual photon spectrum from 10 to 200 MeV, and assuming for the photo-disintegration of Helium a mean cross-section of $1{\cdot}8 \times 10^{-27}$ cm.^{2}, [7] and for the γ, p cross-section in emulsion nuclei a mean value of 2×10^{-26} cm.^{2}, [8], we estimate the mean free path for the break up of the α-particle and the target nucleus to be about 5 metres and 100 metres, respectively. From this it can be seen that among all the 176 interactions included for the angular measurement there should be six events of (0 + 2) α type (where both shower particles should be within the cut off angle) due to coulomb interaction. The rest as well as the α in–α out events should be due to nuclear rather than coulomb interaction.

3.4. Characteristics of Interactions in which 0, 1 or 2 Protons Interact

From the arguments given in 3.2, it is clear that we can separate the α-stars into groups defined by the number of protons which have taken part in the interactions. Classified in this manner, we have:

A Group—34 examples with at least two shower particles at angles less than 2×10^{-2} radians (including 14 cases of "α in–α out");

B Group—63 examples with one shower particle at less than 2×10^{-2} radians; and

C Group—73 examples with no shower particle within the cut off angle.
Total—170.

We have excluded from this and from all the ensuing analysis on *nuclear interactions*, 6 events of the type (0 + 2) α (with both shower particles inside the cut off angle) which we attribute to coulomb interactions.

The multiplicity and the heavy prong distributions of stars classified in (A), (B) and (C) are represented in Figs. 4 and 5.

Separate histograms are included for the "α in–α out" events where the emerging α-particle is considered equivalent to two singly charged particles.

In this we have also included two other examples of "α in–α out" observed in a less systematic survey. The mean values of the multiplicity $< n_s >$ and the heavy prong number $< N_h >$ as well as the mean number of 'secondary shower particles' (type *b*) $< n'_s >$ per star for the various groups are summarised in Table II.

TABLE II

	6·2 BeV Proton Stars	All α-stars	A No Proton Interacting		B One Proton + 0, 1 or 2 neutrons inter-acting	C At least two protons inter-acting
			α in–α out (one neutron inter-acting) (*a*)	The rest (one or two neutrons inter-acting) (*b*)		
No. of events	99	170	13	21	63	73
Mean No. of shower particles per star $<n_s>$	2·6	8·0	3·1	5·6	7·0	11·0
Mean No. of secondary shower particles per star $<n'_s>$	2·6	7·5	1·1	3·6	6·0	11·0
Mean No. of heavy prongs per star $<N_h>$	6·4	7·7	2·5	2·1	5·6	12·7

In Group A (*a*) stars we know that only one neutron has interacted and the emerging doubly charged particle should be a He^3. Therefore, almost all these events should represent edge collisions. This argument is further strengthened by the fact that the mean number of heavy prongs associated with these stars is only 2·5. We may conclude that subject to an appreciable statistical uncertainty, in a single neutron-nucleon collision at the energies we are dealing with, the mean number of secondary charged shower particles produced is 1·1. This may be compared with the value of 2·6 averaged for all types of collisions produced by 6·2 BeV protons.

It has been shown in 3·2 that the corrected total number of protons that have not interacted is 151. We remove from this the six (0 + 2) α events of coulomb interaction; there remain 139. If we now assume symmetry in

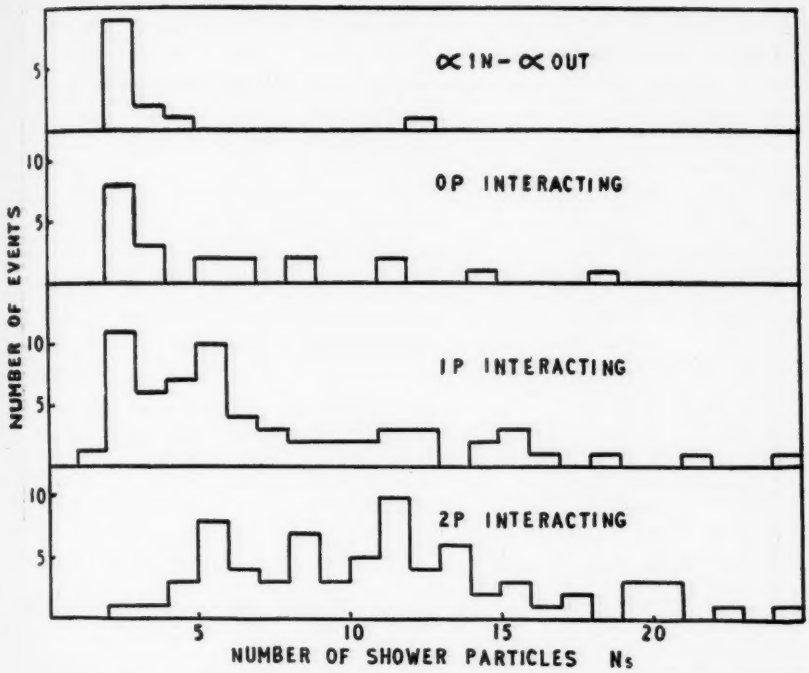

FIG. 4. The shower particle distribution of α-induced interactions classified as to whether 0, 1 or 2 protons have taken part in collisions. The shower particle distribution of α in–α out events is also given.

behaviour between neutrons and protons taking part in nuclear interactions, then the mean number of nucleons taking part in collisions per α-star is:

$$\frac{170 \times 4 - 139 \times 2}{170} = 2{\cdot}4.$$

From this we find that the mean number of secondary shower particles per nucleon averaged for all α-stars is $7{\cdot}5/2{\cdot}4 = 3{\cdot}1$ for a median energy of 10 BeV/nucleon. This should be compared with the value of 2·6 for 6·2 BeV proton stars.

We would like to point out here that from a knowledge of the number of disintegrations where 0, 1 or 2 protons have taken part in interactions, it is possible to estimate the number of events in which 1, 2, 3 or 4 nucleons should have participated. This information together with a nuclear density distribution obtained from other experiments may permit one to calculate the nucleon-nucleon cross-section at very high energies. Such an attempt has

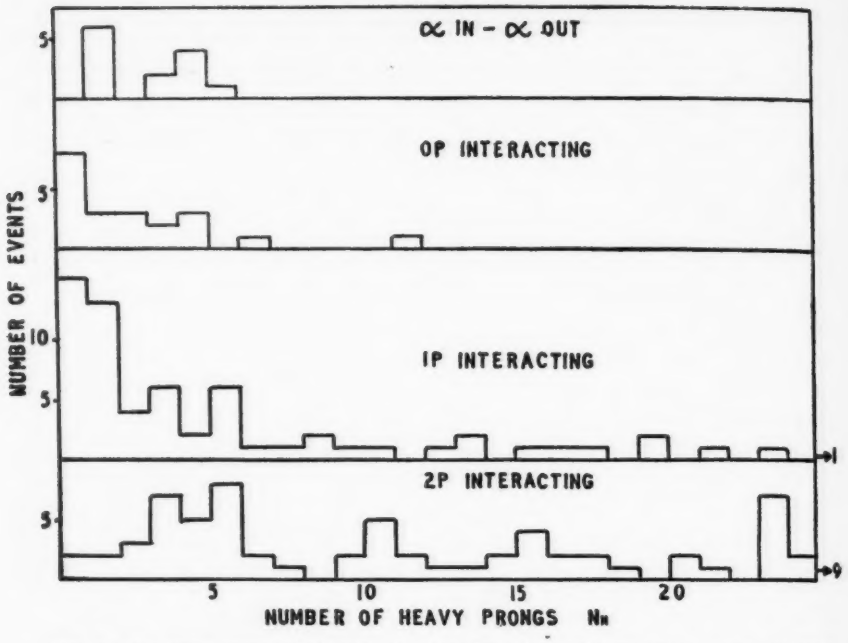

FIG. 5. The heavy prong distribution is given for α-induced interactions when classified as to whether 0, 1 or 2 protons have interacted. A similar distribution for α in–α out events is also included.

not been made because there is as yet no precise knowledge of the nuclear density distribution.

4. MEAN FREE PATH OF HIGH ENERGY α-PARTICLES AND PROTONS

4.1. MEAN FREE PATH FOR NUCLEAR INTERACTION OF α-PARTICLES IN EMULSION

As stated previously we obtained a total of 242 interactions from a total path length of 40·84 metres. We have shown in 3.3 that the mean free path for coulomb interaction is 5 metres. Therefore, corresponding to the 234 interactions of nuclear origin, we obtain a mean free path $\lambda = 17{\cdot}5 \pm 1{\cdot}1$ cm. ($68{\cdot}9 \pm 4{\cdot}3$ gm./cm.^{2}). (The density of our emulsions estimated from the range of μ-mesons arising from the decay at rest of π-mesons is 3·94 gm./cm.^{2})

There could be two possible sources of error in determining the total track length of the α-particles:

(*a*) Contamination due to slow protons, deuterons and tritons;

(*b*) While testing tracks for their straightness by the use of the eye-piece hair line in the first plate, it is possible that some genuine relativisitic α-particle may be rejected because of local distortion, while if it interacted in the same emulsion, it would have been included. Thus, there could be a bias in favour of α-particles which produce a nuclear disintegration in the first or second emulsions.

It has been shown in 2.2 that the contribution from slow protons, deuterons and tritons is negligible. This can further be tested as follows: We calculate the mean free path taking only tracks with a potential range greater than 10 cm. in the stack. Any appreciable contamination due to P, D, T should now be greatly reduced, for at 10 cm. traversal they will either be brought to rest or show considerable change in grain density. The value $\lambda = 17{\cdot}0 \pm 1{\cdot}7$ cm. which we obtain, does not differ from that obtained by including tracks of shorter potential range. We may state, therefore, that there is no significant contamination by singly charged particles in our selection of primary α-particles.

In order to test whether there could be any systematic bias as suggested in (*b*), we removed the first 2 cm. of track length of every α-particle track as well as the interactions observed in that distance. The mean free path obtained from the rest of the track length should be independent of this bias in selection of tracks and is found to be $16{\cdot}7 \pm 1{\cdot}2$ cm., as compared to $17{\cdot}5 \pm 1{\cdot}1$ cm., obtained without this correction. Thus, the values agree within experimental errors, and indicate no bias in favour of α-particles interacting in the first 2 cm. of track length.

In Table III, we have summarised the mean free path for nuclear interactions of α-particles observed in nuclear emulsions by various authors.

TABLE III

Authors	Method of Scanning	Energy per Nucleon	M.F.P. λ
D. F. Sherman ..	Area scanning	95 MeV	$18{\cdot}1 \pm 1$ cm.
Ceccerelli and Zorn ..	Along the track	90 MeV	$20{\cdot}5 \pm 2{\cdot}5$ cm.
Waddington ..	do.	>500 MeV	$20{\cdot}6 \pm 2{\cdot}2$ cm.
Present experiment ..	do.	>5 BeV	$17{\cdot}5 \pm 1{\cdot}1$ cm.

Using the mean free path for interaction we have obtained, and the composition of the emulsion as supplied by the manufacturers, we calculate an

effective nuclear raidus. We assume a radius $R = r_0 \times A^{1/3}$ for all target nuclei as well as the α-particle (here A denotes the mass number). In this way one obtains the value:

$$r_0 = 1{\cdot}13 \pm 0{\cdot}04 \times 10^{-13} \text{ cm.}$$

This value is very close to that obtained from recent work on high energy electron scattering,[10] and mesic X-rays.[11]

4.2. Mean Free Path of 6·2 BeV Protons in Emulsion

When scanning for nuclear interactions produced by 6·2 BeV protons of the Berkeley Bevatron, using the 'along the track' method, we obtained 35·69 metres of track length and 103 interactions. From this we get for the mean free path a value of $34{\cdot}7 \pm 3{\cdot}4$ cm. in emulsion. We now used the value of $0{\cdot}78 \pm 0{\cdot}24 \times 10^{-13}$ cm. for the size of the proton obtained by Hofstadter *et al.*[9] from electron scattering experiments and calculated the value of r_0 as described in 4.1. We get $r_0 = 1{\cdot}01 \pm 0{\cdot}11 \times 10^{-13}$ cm., in agreement with the value of $1{\cdot}13 \pm 0{\cdot}04 \times 10^{-13}$ cm. obtained from the mean free path of nuclear interaction of α-particles (4.1).

4.3. Mean Free Path of Nucleons in Nuclear Matter

Though at present we do not have any precise knowledge of the nuclear density distribution, it is still possible with our experimental data to infer an upper limit to the mean free path of nucleons in nuclear matter. This is done in the following manner:

Stars associated with 9 or more heavy prongs represent collisions of α-particles with the heavy nuclei of silver and bromine in the emulsion. Because of the large number of slow particles associated with the disintegrations it is reasonable to assume that:

(*a*) The majority of these events should have resulted from central or near central collisions with the target nucleus; and

(*b*) As we go to events with greater number of N_h the area involved becomes smaller and will refer more and more to the central portion of the target nucleus.

An estimate of the size of the central area involved can be made from the total α-particle track length, the number of collision events of the required type and the proportion of Ag and Br in emulsions. Here one must take into account the finite size of the α-particle and must choose a value of N_h such that, when the centre of the α-particle lies just within the corresponding central area, the α-particle lies wholly within the nuclear boundary of the target nucleus (Fig. 6). This value of N_h was found to be $\geqslant 15$. We have assumed in

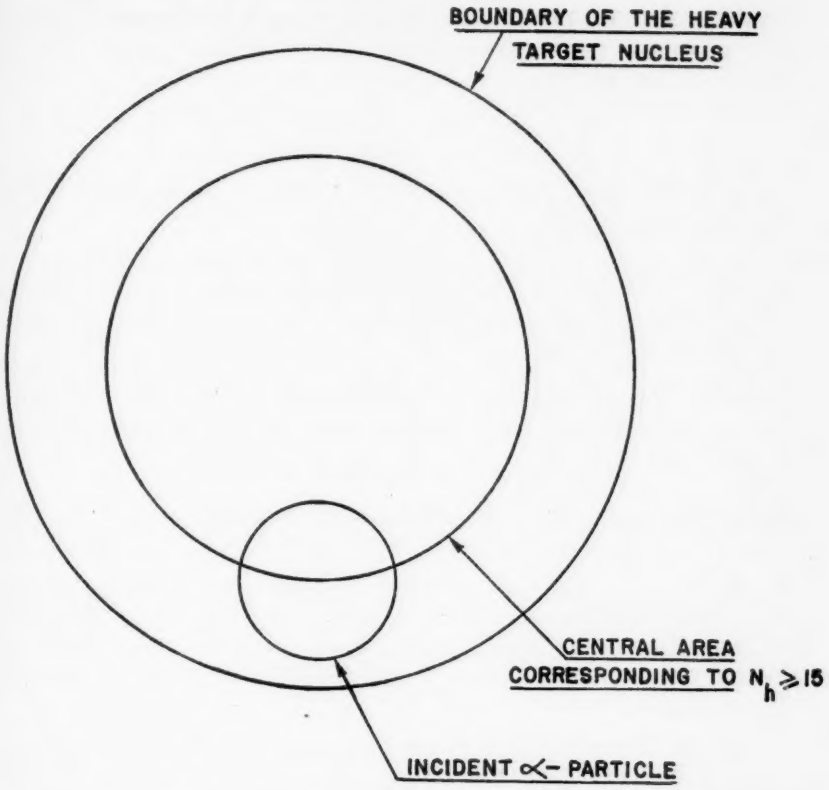

FIG. 6. Diagram illustrating the relative positions of the incident α-particle and the target nucleus in central collisions (corresponding to events with $N_h \geqslant 15$).

these calculations that the nuclei (both the target as well as the α-particle) are spherical and their radii given by the relation $R = r_0 A^{1/3}$, where $r_0 = 1 \cdot 13 \times 10^{-13}$ cm. We then calculated the mean distance in nuclear matter traversed by the α-particle after taking into consideration the different sizes and numbers of silver and bromine nuclei and this is found to be $6 \cdot 86 \times 10^{-13}$ cm. We observed among 39 stars with $N_h \geqslant 15$ included for angular measurements, 9 protons emerging without taking part in collisions. Using this information and the mean distance of nuclear matter traversed by the α-particle the mean free path for nucleon-nucleon collisions in nuclear matter λ_N is found to be $3 \cdot 2 \times 10^{-13}$ cm. Though it may be true that on the average stars with $N_h \geqslant 15$ result from central collisions with the heavy target nuclei, this will not be the case in individual events. It is certain that our selection

of stars will contain some edge collisions where a portion of the incident α-particle may not traverse any nuclear matter and still result in $N_h \geqslant 15$. Therefore, the value of $3{\cdot}2 \times 10^{-13}$ cm. we obtain here for the mean free path for nucleon-nucleon collisions in nuclear matter will be an upper limit only.

5. CONCLUSIONS

The main conclusions deduced from the above investigation may be summarised as follows :

(*i*) From the angular distribution of shower particles associated with interactions produced by α-particles of energy greater than 5 BeV/nucleon, it is shown that singly charged relativistic particles ejected at angles less than 2×10^{-2} radians consist of :

(*a*) 95% of protons which originally formed part of the incident α-particle and did not participate in any collision processes; and

(*b*) 5% of secondary shower particles.

This permits separation of protons that have not collided with any part of the traget nucleus from the remaining shower particles without much ambiguity.

(*ii*) The mean free path for nuclear interaction of α-particles with energies $>$ 5 BeV/nucleon in emulsion is found to be $17{\cdot}5 \pm 1{\cdot}1$ cm. ($68{\cdot}9 \pm 4{\cdot}3$ gm./cm.^{2}). Assigning both to the incident α-particle and the target nuclei a radius $R = r_0 A^{1/3}$, an effective nuclear radius $r_0 = 1{\cdot}13 \pm 0{\cdot}04 \times 10^{-13}$ cm. is obtained.

(*iii*) The mean free path for nuclear interaction of protons of 6·2 BeV energy in emulsions is $34{\cdot}7 \pm 3{\cdot}4$ cm.

(*iv*) Assuming that events with $N_h \geqslant 15$ result from central collisions of α-particles with silver and bromine of the emulsions, an upper limit to the mean free path of nucleons in nuclear matter λ_N has been calculated. We find $\lambda_N < 3{\cdot}2 \times 10^{-13}$ cm.

6. ACKNOWLEDGEMENT

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